DOI: 10.1002/asia.201100092

Diphosphine Capsules for Transition-Metal Encapsulation

Tehila S. Koblenz,[a] Henk L. Dekker,[b] Chris G. de Koster,[b] Piet W. N. M. van Leeuwen,[a] and Joost N. H. Reek*[a]

Abstract: Self-assembly and characterization of novel heterodimeric diphosphine capsules formed by multiple ionic interactions and composed of one tetracationic diphosphine ligand and one complementary tetraanionic calix[4]arene are described. Encapsulation of a palladium atom within a diphosphine capsule is achieved successfully by using the metal complex of the tetracationic diphosphine ligand for the assembly process. In this templated approach to metal encapsulation, the transition-metal complex is an integrated part of the capsule with the transition metal located inside the capsule and is not involved in the assembly process. We present two approaches for capsule assembly by mixing solutions of the precharged building blocks in methanol and mixing solutions of the neutral building blocks in methanol. The scope of the diphosphine capsules and the metallodiphosphine capsules is easily extended by applying tetracationic diphosphine ligands with different backbones (ethylene, diphenyl ether, and xanthene) and cationic binding motifs (p-C_6H_4-CH_2-ammonium, m-C_6H_4-ammonium, and m-C_6H_4-guanidinium). These tetracationic building blocks with different flexibilities and shapes readily associate into capsules with the proper capsular structure, as is indicated by ^{1}H NMR spectroscopy, 1D NOESY, ESI-MS, and modeling studies.

Keywords: calixarenes · ionic interactions · palladium · phosphine ligands · supramolecular chemistry

Introduction

Supramolecular capsules are composed of two or more, not necessarily identical, building blocks programmed to self-assemble in solution into the desired structure.[1a–f] The building blocks of the capsule have a similar size, complementary functional groups, and associate by means of multiple reversible noncovalent interactions such as hydrogen bonds, metal–ligand, and ionic interactions.[2–4] A wide variety of homo- and heterocapsules based on functionalized calixarenes, resorcinarenes (cavitands), and other building blocks have been reported. The encapsulation properties of these hosts enable their utilization as nanosized reactor vessels (nanoreactors), and so far their use has been explored for the stabilization of reactive intermediates, for organic transformations, and for catalysis.[1a,b,g–r,2h,3h]

Reports of capsules based on ionic interactions are in a minority compared to the hydrogen-bonded capsules. Timmerman, Crego-Calama, and co-workers reported ionic-based capsules that consisted of one tetrasulfonated calix[4]arene and one tetracationic Zn^{II} porphyrinate (Figure 1a).[4b,c,g] Schrader and co-workers studied ionic-based capsules composed of one tetraanionic calix[4]arene and one tetracationic calix[4]arene (Figure 1b).[4a,g] Verboom and co-workers reported ionic-based capsules constituted of two tetracationic cavitands and four monovalent anions (Figure 1c).[4e] In contrast to hydrogen-bonded capsules, ionic-based capsules are generally stable in polar solvents, do not require an external guest (but contain solvent) as a template for capsule formation, and undergo an exchange process fast on the NMR spectroscopic timescale between the free and capsule-bound building blocks.

Many reactions of interest require well-defined transition-metal complexes as a catalyst, and the activity and selectivity of these catalysts are determined to a large extent by the ligand associated with the metal. So far only a few supramolecular complexes have been reported in which the cata-

[a] Dr. T. S. Koblenz, Prof. Dr. P. W. N. M. v. Leeuwen, Prof. Dr. J. N. H. Reek
Homogeneous and Supramolecular Catalysis
Van't Hoff Institute for Molecular Sciences
University of Amsterdam
Postbox 94720, 1090 GS Amsterdam (The Netherlands)
Fax: (+31) 020-5255604
E-mail: J.N.H.Reek@uva.nl

[b] H. L. Dekker, Prof. Dr. C. G. d. Koster
Mass Spectrometry of Biomacromolecules
Swammerdam Institute for Life Sciences
University of Amsterdam
Postbox 94720, 1090 GS Amsterdam (The Netherlands)

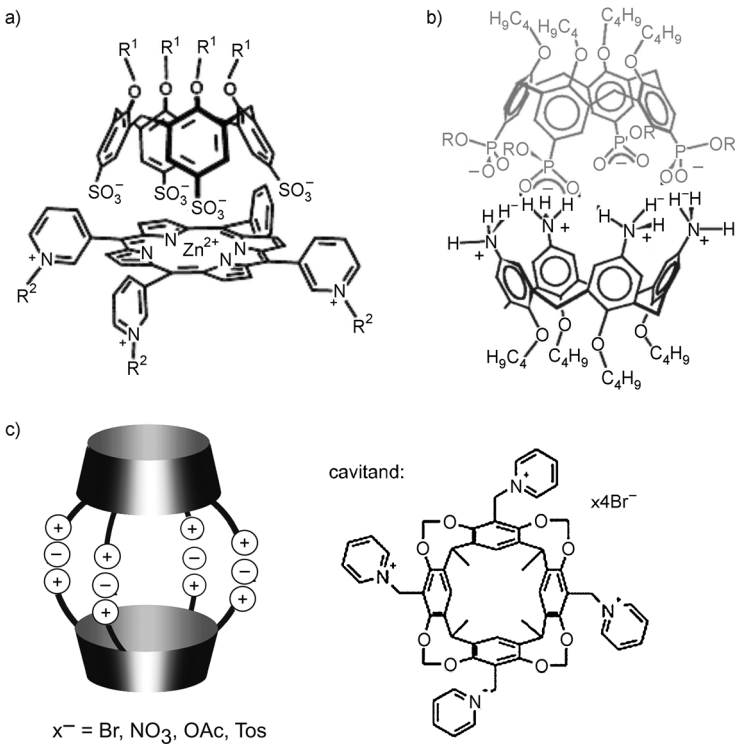


Figure 1. Supramolecular capsules based on ionic interactions and composed of a calix[4]arene and a) a Zn^{II} porphyrinate, b) two calix[4]arenes, and c) two cavitands and four anions.

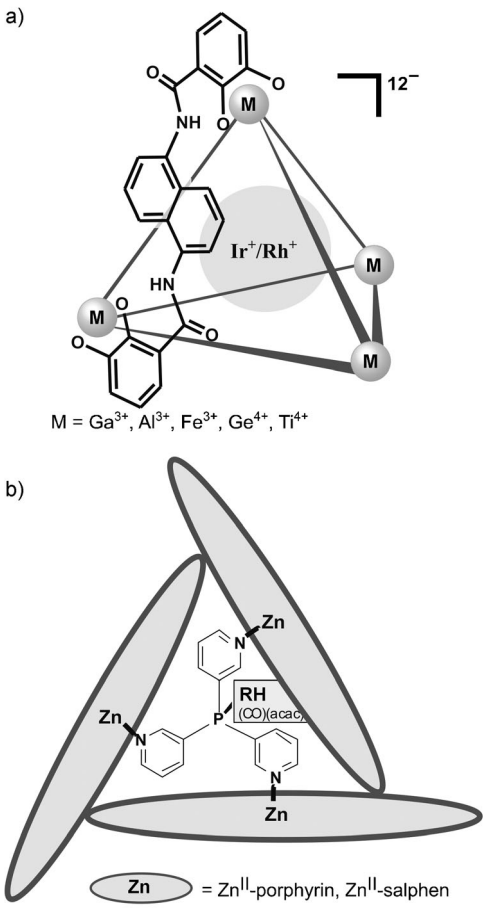


Figure 2. Encapsulated transition-metal catalysts within a) a tetrahedral coordination cage $[M^4\mathbf{L}_6]^{12-}$ and b) a hemispherical ligand-template capsule.

lytic potential of an encapsulated transition metal has been explored. Raymond, Bergman, and co-workers encapsulated cationic iridium and rhodium complexes inside the chiral tetrahedral coordination cage $[M^4\mathbf{L}_6]^{12-}$ through nondirectional noncovalent bonds (Figure 2a). Encapsulation of the catalyst resulted in substrate selectivity on the basis of size and shape in the C–H bond activation of aldehydes and the isomerization of allylic alcohols.[3j,6a,b] Reek and co-workers introduced a templated approach for the encapsulation of ligands and their metal complexes, in which the template ligands have a bifunctional character in that they coordinate to the active metal center and function as a template for the capsule formation.[5,6c–j] Pyridylphosphines are successful template ligands as the nitrogen atoms of the pyridyl groups selectively coordinate to Zn^{II}–porphyrins or Zn^{II}–salphens, thereby resulting in a hemispherical ligand–template capsule around the transition metal (Figure 2b). Such encapsulated rhodium complexes were shown to have unusual reactivity and selectivity in the hydroformylation of terminal and internal alkenes.

We have previously communicated an ionic-based capsule composed of a tetracationic xantphos-type diphosphine and a tetraanionic calix[4]arene.[5] Encapsulation of a palladium atom within this capsule is achieved by using the metal complex of the tetracationic diphosphine ligand for the assembly process (Figure 3). In this templated approach to metal encapsulation, the transition-metal complex is an integrated part of the capsule with the transition metal located inside the capsule and it is not involved in the assembly process.[3j,6a–h] Hence, the encapsulated metal is still available for cata lytic transformations. Transition-metal complexes that contain diphosphine ligands represent an important class of catalysts, and changes in ligand structure have important

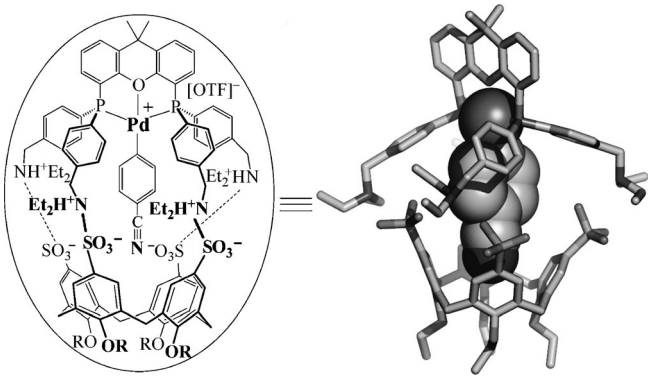


Figure 3. Encapsulation of a palladium species within an ionic-based capsule composed of a Pd(diphosphine) complex and a calix[4]arene: molecular and modeled structures.

consequences for their application in catalysis.[7] In that respect, we were interested if the structure of the bidentate ligand has a large influence on the formation of the capsule. Here, we report diphosphine capsules based on a tetracationic diphosphine and a tetraanionic calix[4]arene. To show the versatility of the diphosphine capsules, we used various tetracationic diphosphines with different backbones (ethylene, diphenyl ether, and xanthene) and different binding motifs (p-C_6H_4-CH_2-ammonium, m-C_6H_4-ammonium, and m-C_6H_4-guanidinium). In addition, we report the formation and characterization of the metallodiphosphine capsules based on palladium complexes of the tetracationic diphosphines.

Results and Discussion

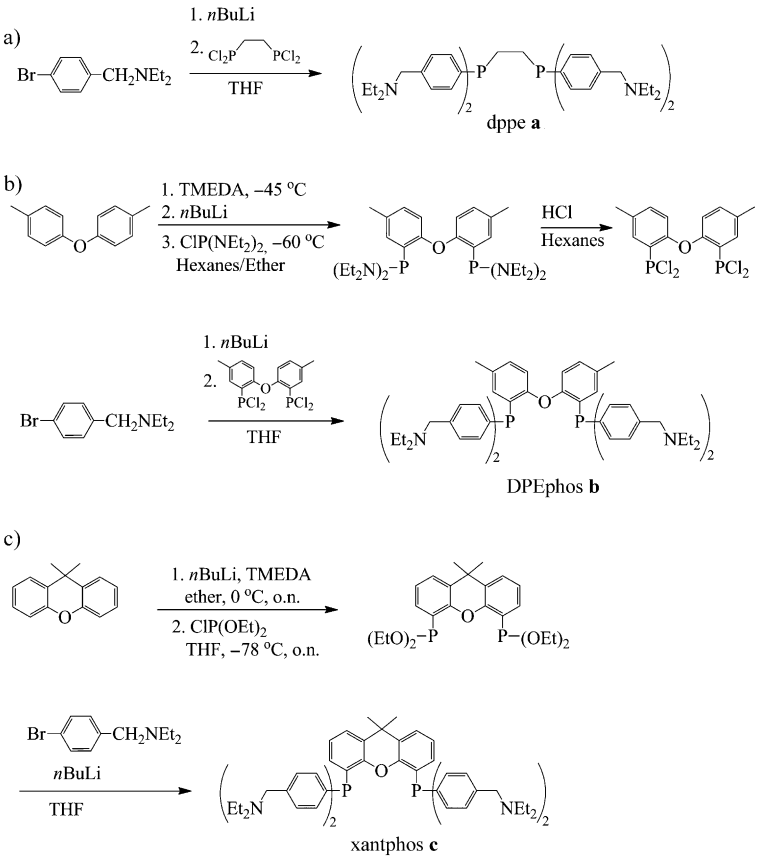
Capsules Based on Cationic Diphosphines: Backbone Variation

We set out to study capsules composed of tetracationic diphosphines and tetraanionic calix[4]arenes.[5] The tetracationic diphosphines used here have different shapes and flexibility properties as a result of their different backbones, that is, ethylene (dppe), diphenyl ether (DPEphos), and xanthene (xantphos).

Synthesis

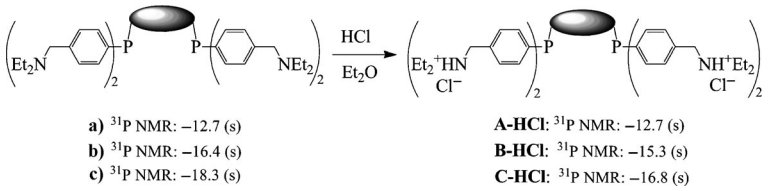
The cationic charges on the diphosphine ligands were created by functionalizing the four phenyl groups on the phosphorus atoms. The tetrakis-ammonium diphosphine ligands **A**, **B**, and **C** were prepared from the corresponding tetrakis-amine precursors **a**, **b**, and **c**. Tetrakis(p-diethylbenzylamine)-dppe **a**, tetrakis(p-diethylbenzylamine)-DPEphos **b**, and tetrakis(p-diethylbenzyl amine)-xantphos **c** were prepared by the reaction of the lithiated product of p-bromobenzyldiethylamine with a phosphorus electrophile, that is, the corresponding bis-dichlorophosphines or diphosphonite (Scheme 1).[8] Reaction of the commercially available 1,2-bis(dichlorophosphino)ethane with the lithiated product of p-bromobenzyldiethylamine gave the tetrakis(p-diethylbenzylamine)-dppe **a** in 60% yield (Scheme 1a).[9] The synthesis of the precursor 2,2′-bis(dichlorophosphino)-4,4′-dimethyldiphenyl ether was carried out as reported by van Leeuwen and co-workers.[10] First, the bis-diethylamino phosphane was prepared by lithiation of the 4,4′-dimethyldiphenyl ether backbone and a subsequent reaction with $ClP(NEt_2)_2$. Next, the bis-dichlorophosphine compound was prepared by reaction with HCl. Reaction of the bis-dichlorophosphine with the lithiated product of p-bromobenzyldiethylamine gave the tetrakis(p-diethylbenzylamine)-DPEphos **b** in 60% yield (Scheme 1b). Tetrakis(p-diethylbenzylamine)-xantphos **c** was previously reported by van Leeuwen and co-workers and was used in the rhodium-catalyzed hydroformylation reaction in which the rhodium complex of the amphiphilic ligand **c** was recycled by extraction into an acidic aqueous phase.[8a] We have developed an improved synthetic route towards **c**, which involves only two steps instead of five, with an overall yield of 50% (Scheme 1c). The diphosphonite was prepared by lithiation of the xanthene backbone and a subsequent reaction with $ClP(OEt)_2$.[8b–d] Reaction of the diphosphonite with the lithiated product of p-bromobenzyldiethylamine gave the tetrakis(p-diethylbenzylamine) xantphos **c**.[11]

Selective N-protonation of tetrakis(p-diethylbenzyl amine)-diphosphines **a**, **b**, and **c** in diethyl ether resulted in the corresponding tetrakis(p-diethylbenzylammonium)-diphosphine ligands **A-HCl**, **B-HCl**, and **C-HCl** (Scheme 2).[5] The electronic effect of the ammonium groups of **A-HCl**, **B-**



Scheme 1. Synthesis of tetrakis(p-diethylbenzylamine)diphosphines of a) the dppe-type **a**, b) DPEphos-type **b**, and c) and xantphos-type **c**.

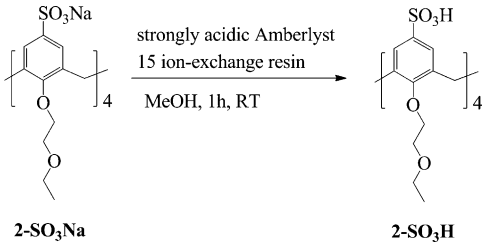
CHEMISTRY
AN ASIAN JOURNAL



Scheme 2. Selective N-protonation of **a**, **b**, and **c** to give the tetrakis(*p*-diethylbenzylammonium)diphosphines **A-HCl**, **B-HCl**, and **C-HCl**.

HCl, and **C-HCl** on the phosphorus atoms is negligible because of the presence of the benzylic methylene spacer. Indeed, $^{31}P\{^{1}H\}$ NMR spectroscopic data confirm that the phosphines are barely affected by the electron-withdrawing ammonium groups (see Scheme 2).[8a,11]

The tetraanionic building block tetrasulfonatocalix[4]arene tetrasodium salt **2-SO$_3$Na** was prepared according to a literature procedure and was subsequently acidified to give the tetrasulfonic acid calix[4]arene **2-SO$_3$H** (Scheme 3).[4b,12]

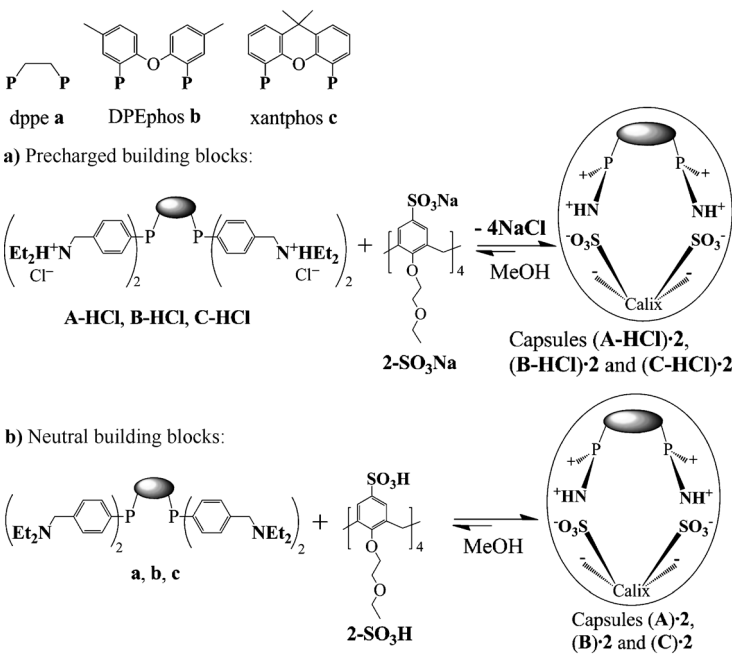


Scheme 3. Acidification of tetrasulfonatocalix[4]arene tetrasodium salt **2-SO$_3$Na** to give the tetrasulfonic acid calix[4]arene **2-SO$_3$H**.

During the synthesis of the tetrasodium salt, we did not succeed in isolating the corresponding tetraacid prior to neutralization. Fortunately, exchange of the sodium cations of **2-SO$_3$Na** with protons was easily achieved with the strongly acidic Amberlyst 15 ion-exchange resin to give **2-SO$_3$H**. All new compounds described here have been characterized by NMR spectroscopy and mass spectrometry (see the Experimental Section).

Self-Assembly

The heterodimeric diphosphine capsules **A·2**, **B·2**, and **C·2** consist of the tetracationic diphosphines **A**, **B**, and **C**, and the complementary tetraanionic calix[4]arene **2**. Self-assembly of these ionic-based capsules was achieved simply by mixing solutions of the corresponding building blocks in methanol. Capsule formation was evidenced by NMR spectroscopy and mass spectrometry. We have developed two approaches for capsule assembly. The first approach involves mixing of the precharged building blocks: for example, tetraammonium diphosphine **A-HCl** and tetrasulfonatocalix[4]-arene tetrasodium salt **2-SO$_3$Na** to give capsule **(A-HCl)·2** (Scheme 4a). Capsules **(B-HCl)·2** and **(C-HCl)·2** were prepared in a similar fashion. All the capsules were instantaneously formed upon mixing methanol solutions of the building blocks and contain four equivalents of the corresponding NaCl salt. The second approach involved mixing of the neutral building blocks: for example, tetraamine diphosphine **a** and tetrasulfonic acid calix[4]arene **2-SO$_3$H** to give capsule **(A)·2** (Scheme 4b). Capsules **(B)·2** and **(C)·2** were prepared in a similar fashion. Upon mixing solutions of the neutral building blocks in methanol, the tetrasulfonic acid calix[4]arene quantitatively protonated the tetraamine diphosphines.[4f,h] The charged building blocks assemble into capsules **(A)·2**, **(B)·2**, and **(C)·2** without salt formation as a side product. Capsules are more stable, that is, they have a higher association constant, when no salt is present in solution.[13] Still, in both approaches the capsules are in equilibrium with their charged and/or neutral building blocks. All diphosphine-based capsules appeared to be soluble and stable in methanol, as will be clear from the evidence presented in the next section.



Scheme 4. Self-assembly of capsules **A·2**, **B·2**, and **C·2** by the use of a) precharged and b) neutral building blocks.

Characterization

The evidence for the formation of the diphosphine-based capsules **A·2** and **B·2**, composed of dppe- and DPEphos-type ligands **A** and **B**, is similar to that obtained for capsule **C·2** based on the xantphos-type ligand **C**, which was previously reported.[5] As can be seen in Figure 4 and Table 1, the ^{1}H NMR spectra of capsules **A·2**, **B·2**, and **C·2** in CD_3OD show sharp resonances and large upfield shifts for the diethylammoniummethyl substituents, $CH_2NH^{+}(CH_2CH_3)_2$ with

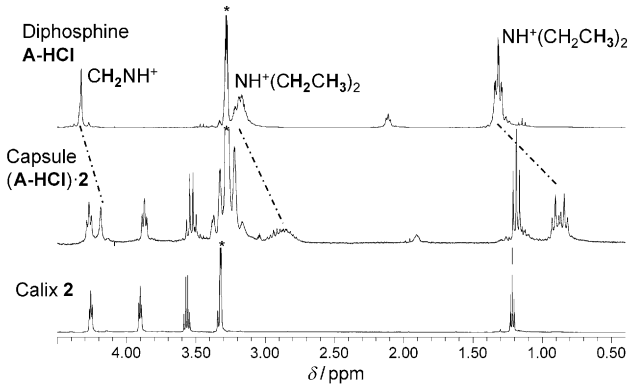


Figure 4. ^{1}H NMR spectra in CD_3OD at 20 °C. Top: **A-HCl** (dppe); middle: capsule **(A-HCl)·2** (**A**/**2** = 2:3, [**A**] = 2 mM); bottom: **2-SO$_3$Na**. Asterisks indicate solvent signals.

Table 1. Upfield shifts ($\Delta\delta$) for the $CH_2NH^+(CH_2CH_3)_2$ protons of the diphosphine capsules with respect to the corresponding free diphosphines **A-HCl**, **B-HCl**, and **C-HCl**; the association constants (K) and the Gibbs free energy of the corresponding diphosphine capsules (ΔG).

Capsule	$\Delta\delta(CH_2CH_3)$[a,b] [ppm]	$\Delta\delta(CH_2CH_3)$[a,b] [ppm]	$\Delta\delta(CH_2N)$[a,b] [ppm]	K[a] [M^{-1}]	ΔG[c] [kJ mol^{-1}]
dppe: **(A-HCl)·2**	0.46	0.31	0.15	3×10^4	25.5
DPEphos: **(B-HCl)·2**	0.42	0.32	0.20	8×10^4	28.0
xantphos: **(C-HCl)·2**	0.43	0.33	0.25	6×10^4	27.3

[a] Measured in CD_3OD at 298 K. [b] **(A-C)**/**2** = 1:3, capsules assembled from the pre-charged building blocks. [c] Gibbs free energy calculated according to $\Delta G = -RT\ln K$.

respect to those of the corresponding free diphosphines **A**, **B**, and **C**. The chemical shifts of the other protons are less affected ($\Delta\delta < 0.20$ ppm). The upfield shifts point to partial inclusion of the diethylammoniummethyl substituents inside the hydrophobic cavity of the capsules.[4c,5]

^{1}H NMR spectroscopic titrations were carried out in CD_3OD (298 K) and provided stability constants of $K_{\mathbf{A}\cdot\mathbf{2}} = 3\times10^4\,M^{-1}$, $K_{\mathbf{B}\cdot\mathbf{2}} = 8\times10^4\,M^{-1}$, and $K_{\mathbf{C}\cdot\mathbf{2}} = 6\times10^4\,M^{-1}$ for capsules **(A-HCl)·2**, **(B-HCl)·2**, and **(C-HCl)·2**, respectively (Table 1 and Figure 5).[5] The high association constants found for the diphosphine capsules confirm that the diphosphine ligands and the tetrasulfonatocalix[4]arene fit well to form stable capsules at low concentrations. The titration curve fitted to a 1:1 binding model, which is in line with the 1:1 stoichiometry of the capsules. As can be seen in Figure 4, a single set of proton resonances for the free and associated building blocks was observed for capsules self-assembled from charged or neutral building blocks. This indicates a fast exchange process on the NMR spectroscopic timescale between the building blocks that are in the monomeric form (free) and those in the capsular form (bound). Consequently, the lower symmetry of the capsules compared to the calix[4]arene **2** (C_{4v}) and possible changes in ligand conformation upon capsule formation are not apparent in the ^{1}H NMR spectra.[4b]

The 1D NOESY spectra of the heterodimeric capsules **A·2** and **B·2** in CD_3OD display significant negative intermolecular NOE contacts between the $NH^+(CH_2C\mathbf{H_3})_2$ protons of the diphosphines **A** and **B** and the aromatic protons of **2** upon selective saturation of the methyl protons of **A** and **B** (Figure 6). This illustrates that the aryl substituents of the diphosphines and the upper rim of the calix[4]arene are facing one another to form the typical dimeric 1:1 capsular structure. The negative NOE enhancements observed for the capsules confirm their large size.[14] Additional evidence for capsule formation and their stabilities in the gas phase was obtained by electrospray ionization mass spectrometry (ESI-MS).[15] The ESI-MS spectra of capsules **A·2** and **B·2** in CH_3OH show prominent ion peaks of the capsules at m/z 908.95 for $[\mathbf{A\cdot2}+2Na]^{2+}$ and at m/z 981.99 for $[\mathbf{B\cdot2}+H+Na]^{2+}$ (Figure 7). All the ion peaks of the capsule correspond to 1:1 complexes and no ion peaks for higher aggregates were detected. The assignment of the ion peaks of the capsule is

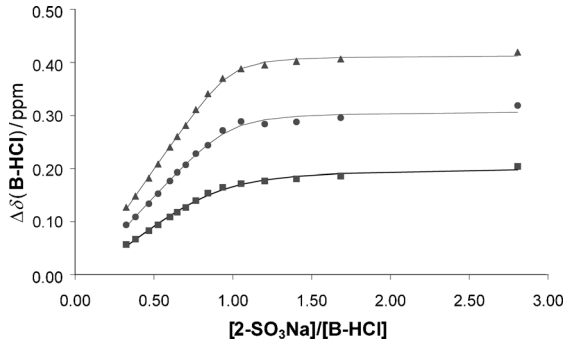


Figure 5. The ^{1}H NMR spectroscopic titration data fitted with a 1:1 binding model for **B-HCl** (DPEphos) with **2-SO$_3$Na** in CD_3OD at 298 K. Data points represent the absolute upfield shifts ($\Delta\delta_B$) of $CH_2NH^+(CH_2CH_3)_2$ protons of **B·2** relative to the chemical shifts of free **B-HCl**: (▲) CH_2CH_3, (●) CH_2CH_3, and (■) CH_2N.

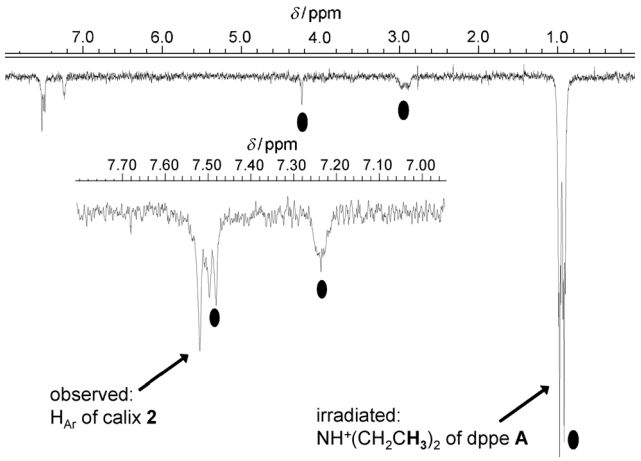


Figure 6. 1D NOESY spectrum of capsule **A·2** in CD_3OD (inset: spectrum enlargement).

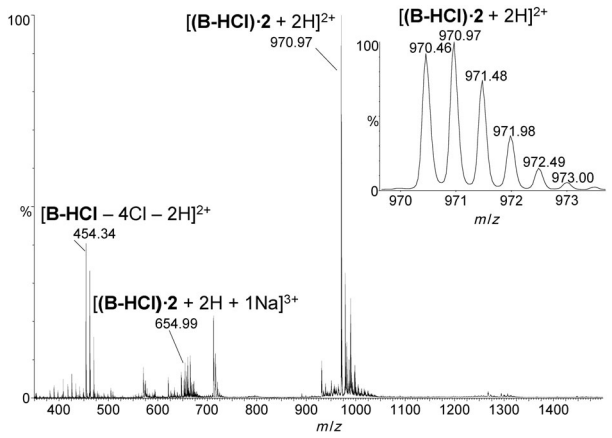


Figure 7. ESI-MS spectrum of capsule **(B-HCl)·2** in CH_3OH (inset: measured isotope pattern).

in agreement with the ESI-MS/MS collision-induced dissociation experiments, upon which the isolated ion peak of the capsule (partly) disappeared and product ion peaks appeared that correspond to the capsule building blocks. These MS/MS experiments reveal the gas-phase stability of the capsule.

Structure

Successful formation of stable supramolecular capsules with proper capsular structures requires their building blocks to be preorganized, that is, thoroughly programmed for the self-assembly process. In general, the building blocks should have comparable sizes, complimentary shapes, and functional groups, and contain the proper balance between flexibility/rigidity.[4a,h,16a,b] Self-assembly of the heterodimeric capsules **A·2**, **B·2**, and **C·2** is primarily driven by the formation of multiple intermolecular ionic interactions between the cationic diphosphine and the anionic calix[4]arene. The three diphosphines contain the same *p*-diethylbenzylammonium groups but have different backbones: ethylene **A**, diphenyl ether **B**, and xanthene **C**. The molecular size of the diphosphines is quite similar to that of concave rigid calix[4]arene **2**. On the other hand, their shape and conformational rigidity varies, which allows us to have a closer look at the influence of the preorganization properties of the building blocks on the structure and stability of the capsule. The xantphos-type diphosphine **C** has a rigid xanthene backbone, two parallel P–$C_{xanthene}$ bonds, and four cationic benzylic groups that are pointing in the same direction, that is, below the ligand plane, as can be seen in the modeled structure (PM3 level) of **C** (Scheme 5c). Consequently, **C** has a defined concave structure and is preorganized for capsule formation. The modeled structure of capsule **C·2** shows that the two building blocks are complementary and that the capsule has a defined and proper capsular structure (Scheme 5c). The high association constant of capsule **(C-HCl)·2**, $K_{C\cdot2}=6\times10^4\,M^{-1}$ ($\Delta G_{C\cdot2}=27.3\,kJ\,mol^{-1}$), reflects that **C** and **2** form a stable capsule. The conformations of free **C** and bound **C** are similar as a consequence of the rigid **C** and that only rotation around the two P–$C_{xanthene}$ bonds is possible. The diphenyl ether backbone of the DPEphos-type diphosphine **B** has a size similar to that of the xanthene backbone of **C**, but it is flexible because it can rotate around its ether functionality and P–$C_{backbone}$ bonds (Scheme 5b). The ethylene backbone of the dppe-type diphosphine **A** results in a slightly smaller diphosphine compared to **B** and **C** and is flexible because it can rotate around three bonds (Scheme 5a). The diphosphines **A** and **B** are less preorganized for capsule formation compared to **C** because they have no concave structure and their four cationic benzylic groups are pointing in different directions. Nevertheless, the modeled structure of capsules **A·2** and **B·2** show that the diphosphines and the calix[4]arene are complementary and that the capsules have a defined and proper capsular structure (Scheme 5). The high association constants of capsules **(A-HCl)·2** and **(B-HCl)·2** ($K_{A\cdot2}=3\times10^4\,M^{-1}$, $\Delta G_{A\cdot2}=25.5\,kJ\,mol^{-1}$ and $K_{B\cdot2}=8\times10^4\,M^{-1}$, $\Delta G_{B\cdot2}=28.0\,kJ\,mol^{-1}$) reflect their stability. The flexibility of **A** and **B** allows them to adopt the optimal conformation needed to form a stable capsule. The expected larger entropy loss for **A** and **B** relative to **C** does not lead to a major difference in ΔG.

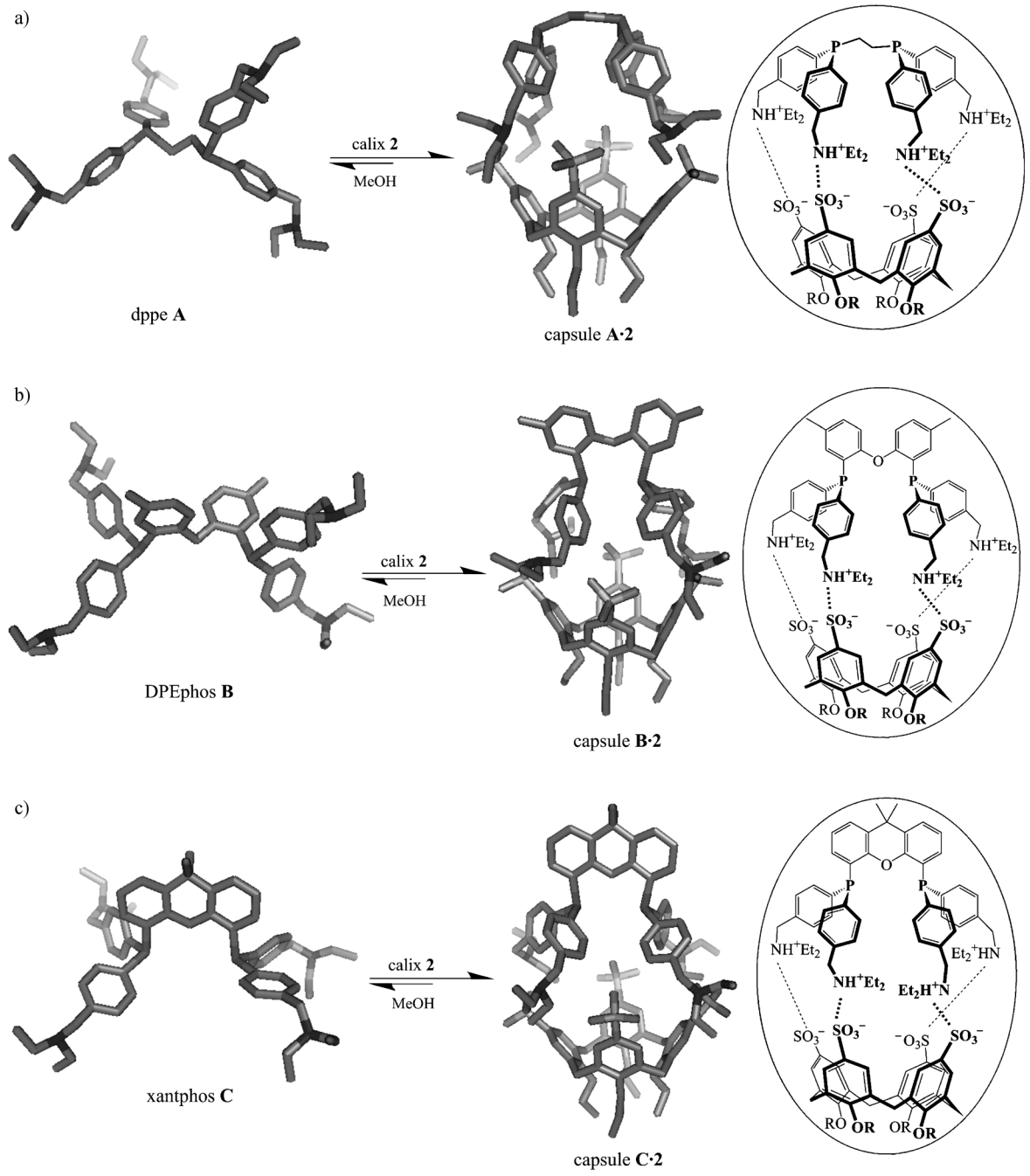
The rigid and concave calix[4]arene **2** fixes the flexible diphosphines **A** and **B** into the proper conformation needed to form a stable capsule. During this fixation, the diphosphine is frozen in its rotation around a few bonds. Hence, only one of the two building blocks needs to be rigid to form a stable capsule with a defined and proper capsular structure.[16b,c] The fine-tuning needed to reach a proper capsular structure is achieved for all the diphosphine capsules by introducing flexibilities at the periphery of the ligand, that is, rotation of the P–Ar and Ar–CH_2 bonds. The modeled structures of **A** and **A·2** show that in both the free and bound state the phosphines are in *trans* conformation, with a C_2 symmetry of **A** (Scheme 5a). We have also noticed that the free electron pairs on the phosphorus atoms of **A·2** are pointing away from the capsule, whereas the free electron pairs on the phosphorus atoms of **B·2** and **C·2** are pointing toward the capsule interior. Clearly, to form a metallodiphosphine capsule, diphosphine capsule **A·2** will have to undergo another conformational change.

Capsules Based on Cationic Diphosphines: Binding Motif Variation

The tetracationic diphosphines studied so far contain a CH_2-ammonium group at the *para* position of the phosphorus aryl groups. In this section we describe tetracationic xantphos-type diphosphines with ammonium and guanidinium groups attached directly to the *meta* position of the phosphorus aryl groups.

Synthesis

The tetrakis(*m*-aniline)-xantphos ligand **d** was prepared by the reaction of the commercially available Grignard reagent 3-[bis(trimethylsilyl)amino]phenylmagnesium chloride with 2,7-di-*tert*-butyl-4,5-bis(dichlorophosphino)-9,9-dimethylxan-

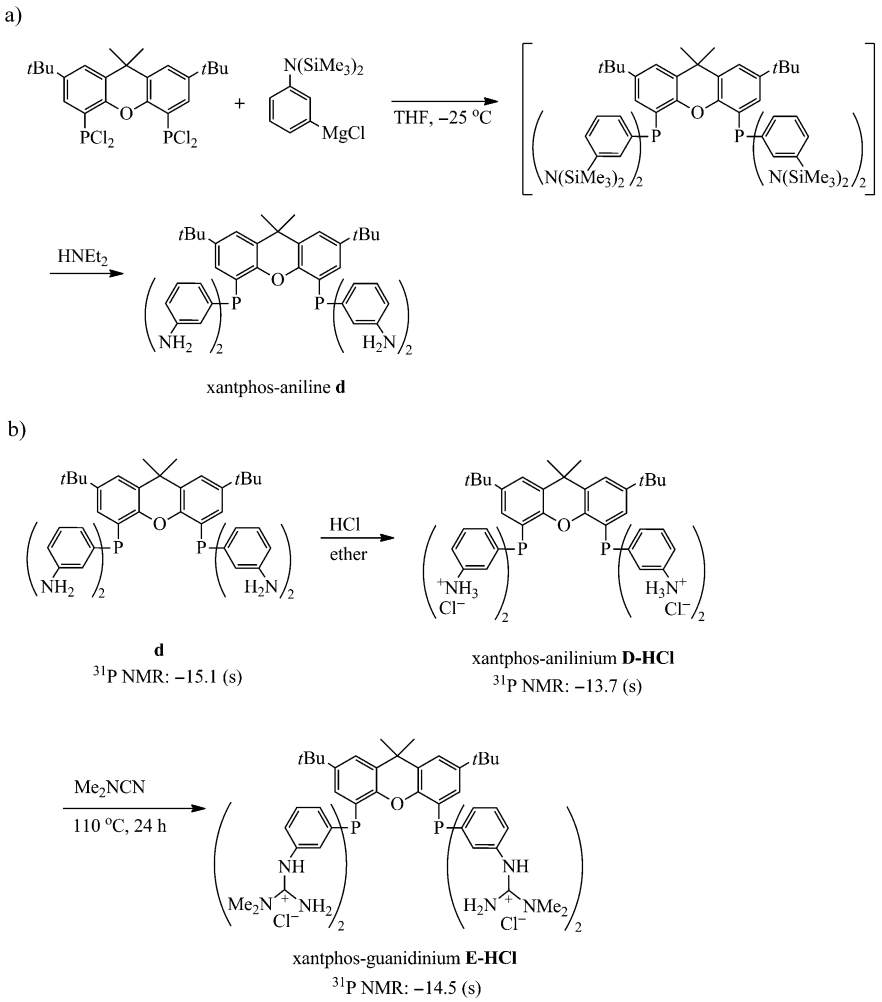


Scheme 5. Self-assembly of diphosphine capsules a) **A·2**, b) **B·2**, and c) **C·2**: modeled and molecular structures.

thene, synthesized from the corresponding bis(diethylamino)phosphonitoxanthene, in 25% yield (Scheme 6a).[17] This reaction requires the use of a dichlorophosphine as the phosphorus electrophile because a diphosphonite is not sufficiently electrophilic to react with the Grignard reagent, which in turn is less nucleophilic than the organolithium compounds. To our surprise, the N-protecting trimethylsilyl groups were removed during the workup procedure, which involved an excess amount of diethylamine, hence no methanolysis step was required.[9a] In a subsequent step, the tetrakis(*m*-aniline)-xantphos **d** ligand was selectively N-protonated by HCl in diethyl ether to yield the corresponding tetrakis(*m*-anilinium)-xantphos **D-HCl** in a quantitative yield (Scheme 6b).

Stelzer and co-workers previously reported the synthesis of 4,5-bis[bis(*m*-*N*,*N*-dimethylguanidiniumphenyl)phosphino]-9,9-dimethylxanthene by palladium-catalyzed P–C coupling of *m*-iodophenylguanidine with the corresponding highly toxic, diprimary phosphine.[18] We prepared tetrakis(*m*-*N*,*N*-dimethylguanidiniumphenyl)-xantphos **E-HCl** in

CHEMISTRY
AN ASIAN JOURNAL



Scheme 6. Synthesis of a) tetrakis(*m*-aniline)-xantphos **d** as well as b) tetrakis(*m*-anilinium)-xantphos **D-HCl** and tetrakis(*m*-guanidiniumphenyl)-xantphos **E-HCl**.

89% yield by treating tetrakis(*m*-anilinium)-xantphos **D-HCl** with an excess amount of dimethylcyanamide (Scheme 6b). The electronic effect of the cationic groups of **D-HCl** and **E-HCl** on the phosphorus atoms is negligible as is suggested by their similar ^{31}P NMR spectroscopic chemical shifts (see Scheme 6b).

Self-Assembly and Characterization

Self-assembly of capsules **D·2** and **E·2** was achieved by mixing methanol or dimethyl sulfoxide (DMSO) solutions of the corresponding precharged building blocks. The ^{1}H NMR spectra of the xantphos-anilinium-based capsule **D·2** in CD_3OD and [D_6]DMSO show sharp resonances. In contrast to, for example, capsule **C·2**, no significant upfield shifts are observed upon capsule formation ($\Delta\delta \leq 0.07$ ppm) because no side chains are present in **D** that change their environment by filling the capsule. The xantphos-guanidinium-based capsule **E·2** shows sharp resonances and significant upfield shifts for the guanidinium substituents, with respect to those of the corresponding free diphosphine **E**: $\Delta\delta(N(CH_3)_2) = 0.51$ ppm in CD_3OD and $\Delta\delta(NH) = 0.55$ ppm in [D_6]DMSO. The upfield shifts point to partial inclusion of the guanidinium moiety inside the hydrophobic cavity of the capsule. A single set of proton resonances for the free and bound building blocks was observed for capsules **D·2** and **E·2**. This indicates a fast exchange process on the NMR spectroscopic timescale between the building blocks that are in the monomeric form (free) and those that are part of the capsule (bound). The ESI-MS spectra of capsules **D·2** and **E·2** in CH_3OH show prominent ion peaks of the capsules at, for example, m/z 914.98 for $[\mathbf{D{\cdot}2}+2\,Na]^{2+}$ and at m/z 711.07 for $[\mathbf{E{\cdot}2}+3\,Na]^{3+}$ (Figure 8). These results support capsule formation and demonstrate their stability in the gas phase.

Capsule stability against bases and acids is important for their further applications in catalysis, and therefore a few preliminary NMR spectroscopic experiments were performed. The addition of cesium carbonate (20 equiv) to a methanol solution of capsule **C·2** resulted in the precipitation of the calix[4]arene **2** and deprotonation of the ammonium-based diphosphine **C**. We assume that the cesium cation is encapsulated within the calix[4]arene.[19] A similar experiment using capsule **E·2** also resulted in the precipitation of **2**, but the guani-

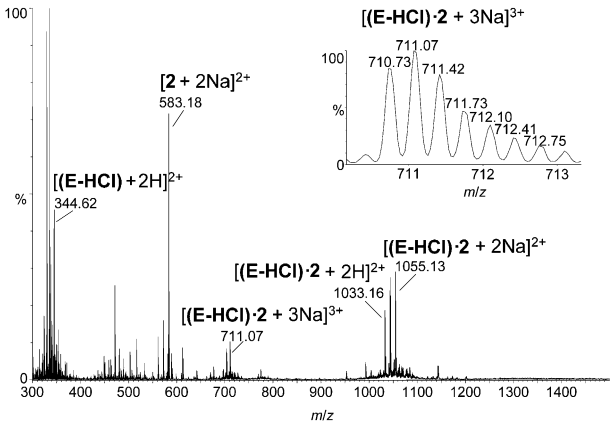


Figure 8. ESI-MS spectrum of capsule **(E-HCl)·2** in CH_3OH (inset: measured isotope pattern).

dinium-based diphosphine **E** remained protonated. This is in line with the strong basicity of guanidine. Upon addition of *p*-toluenesulfonic acid (20 equiv) to capsule **E·2** no precipitation appeared, but judging from the NMR spectra we conclude that the presence of an acid slightly destabilizes the ionic capsule: $\Delta\delta(N(CH_3)_2^+)$ decreased from 0.51 to 0.42 ppm.

Structure

The four positive charges of the xantphos-anilinium ligand **D** are located directly at the *meta* position of the phosphorus aryl groups. The modeled structure (PM3 level) of capsule **D·2** shows a highly symmetrical capsular structure with the four aryl groups situated perpendicular to the capsule equator (Figure 9a). In addition, the ammonium groups are pointing down; each one is situated between two sulfonato groups of the calix[4]arene and interacts with both sulfonato groups. According to molecular modeling studies, moving the ammonium groups from the *meta* to the *para* position is less favorable because the corresponding capsule enforces a twist in the phosphorus aryl groups. Introducing a methylene spacer between the aryl ring and the cationic group does result in stable capsules, as was shown for capsule **C·2**. Hence, a careful design of the building blocks is important.[4a,h,16a,b,20] Unlike the diethylammonium-xantphos ligand **C**, the xantphos-anilinium ligand **D** lacks alkyl substituents on the ammonium groups and still forms a capsule. Hence, the presence of side chains is not a prerequisite for capsule formation.

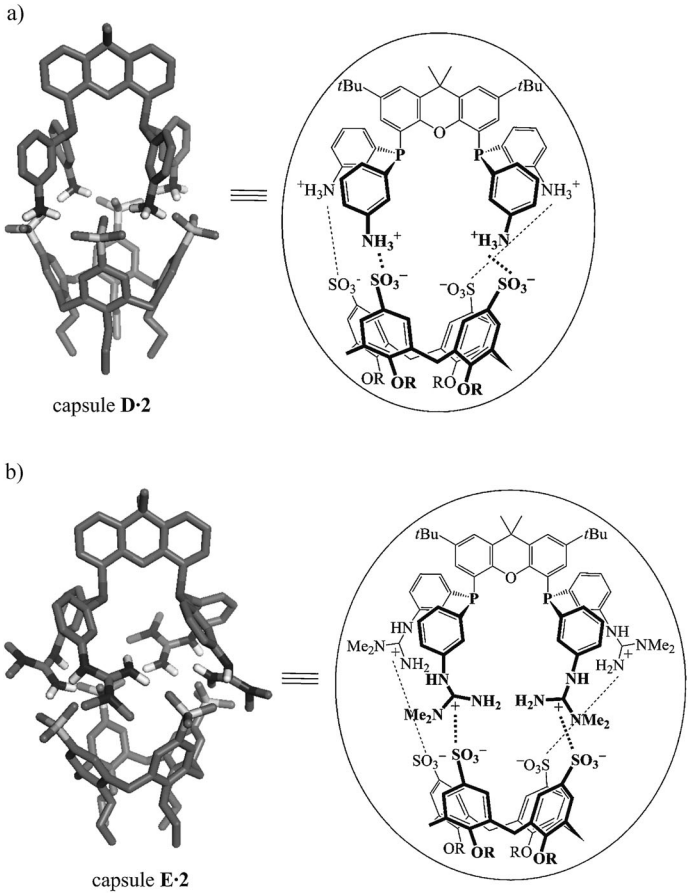


Figure 9. Modeled and molecular structures of diphosphine capsules a) **D·2** and b) **E·2**. The NH hydrogen atoms are visible.

The planar Y-shaped guanidinium group, $[NHC(NH_2)_2]^+$, is known for its ability to form directed hydrogen bonds as well as nondirected ionic interactions, that is, ionic-hydrogen bonds, with, for example, complementary oxoanions such as carboxylates.[4c,21a] The four $[NHC(NH_2)(NMe_2)]^+$ guanidinium groups of the xantphos-guanidinium ligand **E** are located directly on the *meta* position of the phosphorus aryl groups. The modeled structure of capsule **E·2** shows that each guanidinium group is located between two sulfonato groups of the calix[4]arene and interacts with both sulfonato groups (Figure 9b).[2c,21b,c] As a result of the large size of the guanidinium groups, capsule **E·2** is less symmetrical than capsule **D·2**.

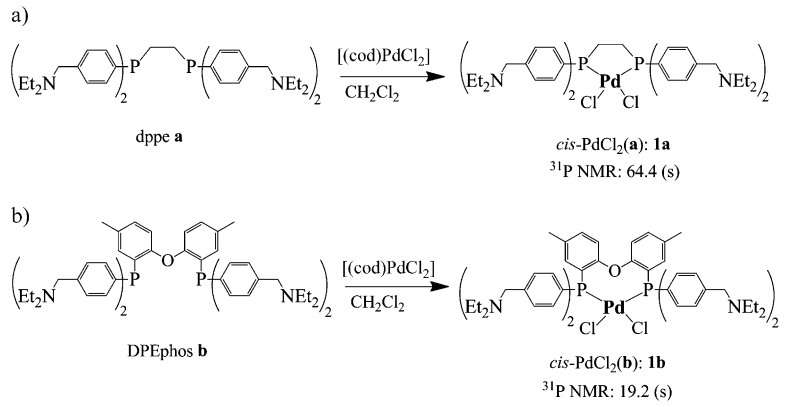
Encapsulation of a Palladium Species

Encapsulation of a transition metal within capsules **A·2** and **B·2** was achieved by using palladium dichloride complexes that contain tetracationic ligands, *cis*-[$PdCl_2$(**A**)] (**1A**) and *cis*-[$PdCl_2$(**B**)] (**1B**).

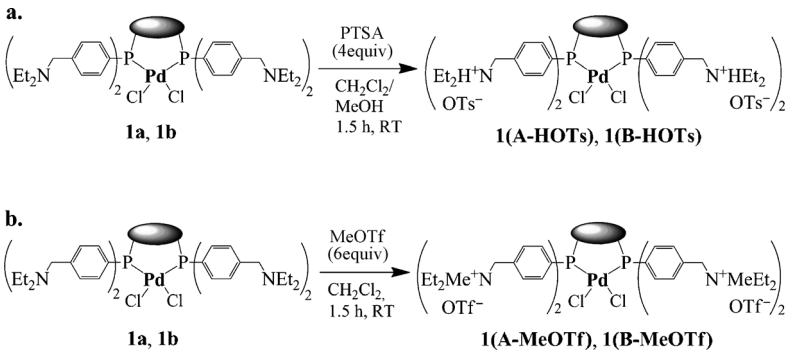
Synthesis

Palladium dichloride complexes *cis*-[$PdCl_2$(**a**)] (**1a**) and *cis*-[$PdCl_2$(**b**)] (**1b**), which contain the tetraamine diphosphine ligands **a** (dppe) and **b** (DPEphos), were prepared in a straightforward manner by the reaction of the metal precursor [$PdCl_2$(cod)] (cod = 1,5-cyclooctadiene) with the corresponding tetraamine diphosphine in dichloromethane (Scheme 7).[10,22] The two palladium complexes were stable in common organic solvents such as chloroform and acetonitrile, but **1b** was unstable in methanol and decomposed rapidly—as is also evident from a color change from yellow to deep brown-purple. Phosphorus NMR spectroscopy displays at least four multiplets at $\delta = -8.0$, 15.7, 20.1, and 29.7 ppm. The deep brown-purple color suggests that Pd^I clusters are formed, probably due to the basic amine groups of the ligand and methanol.[23] Pd^{II} and base in methanol will generate palladium methoxy species, which give palladium hydrides through β-hydrogen elimination. The latter with base gives Pd^0, which dimerizes with Pd^{II} to give strongly colored dimers (or trimers).

The positive charges on the tetraamine diphosphine ligands of **1a** and **1b** are created by N-quaternization by protonation or methylation. Selective N-protonation of **1a** and **1b** was achieved by a reaction with *p*-toluenesulfonic acid (PTSA) to give **1(A-HOTs)** and **1(B-HOTs)**, respectively (Scheme 8a). N-Methylation is preferred over N-protonation because an acidic proton is more labile than an alkylammonium group, and also oxidative addition of HX to the metal can take place. Selective N-methylation of **1a** and **1b** was achieved by a reaction with methyl triflate to yield the tetracationic-diphosphine palladium complexes **1(A-**



Scheme 7. Synthesis of [(tetraamine diphosphine)$PdCl_2$] complexes a) **1a** and b) **1b**.



Scheme 8. Selective N-quaternization of the [(tetraamine diphosphine)$PdCl_2$] complexes **1a** and **1b** by a) toluenesulfonic acid and b) methyl triflate to give the [(tetraammonium diphosphine)$PdCl_2$] complexes **1A** and **1B**.

mixing solutions of the neutral building blocks [(tetraamine diphosphine)$PdCl_2$] complex (**1a** or **1b**) in methanol or dichloromethane and tetrasulfonic acid calix[4]arene **2-SO_3H** (Scheme 9b). After protonation of the tetraamine diphosphine by the acidic calix[4]arene, the now charged building blocks self-assembled into capsules **1(A)·2** or **1(B)·2**, respectively, without salt formation. The salt-free palladium capsules **1(A)·2** and **1(B)·2** hardly dissolved in methanol, unlike the palladium capsules assembled from the precharged building blocks. Addition of 5–10% (v/v) of the cosolvents dichloromethane or water did result in better solubility of the capsules. The four equivalents of salt and the NMe^+ groups of capsules **1(A-MeOTf)·2** and **1(B-MeOTf)·2** probably facilitate capsule solubility in methanol relative to the salt-free capsules **1(A)·2** and **1(B)·2**.

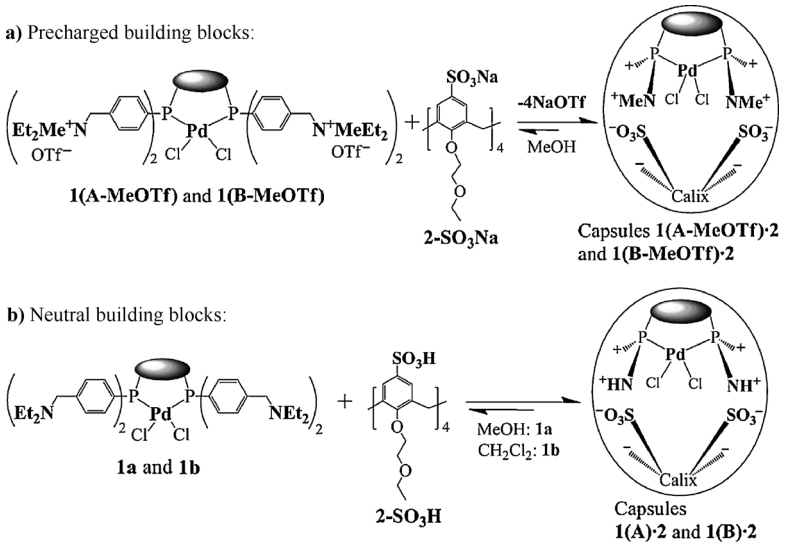
Characterization

The ^1H NMR spectra of the palladium–diphosphine capsules **1A·2** and **1B·2** show upfield shifts for the diethylammoniummethyl substituents, $CH_2N(H/CH_3)^+(CH_2CH_3)_2$, with respect to those of the corresponding free palladium com-

MeOTf) and **1(B-MeOTf)**, respectively (Scheme 8b). Interestingly, after protection of the amines of **1b** by N-quaternization, the palladium complexes **1(B-HOTs)** and **1(B-MeOTf)** were stable in methanol, in contrast to their neutral (i.e., basic) analogue **1b**.

Self-Assembly

Self-assembly of the metallodiphosphine capsules was observed upon mixing solutions of the precharged building blocks in methanol: [(tetraammonium diphosphine)$PdCl_2$] complex, for example, **1(A-MeOTf)**, and tetrasulfonatocalix[4]arene tetrasodium salt **2-SO_3Na** (Scheme 9a). The palladium capsules **1(A-MeOTf)·2** and **1(B-MeOTf)·2** were formed instantaneously and contain four equivalents of the corresponding NaOTf salt. Capsule formation was also accomplished by



Scheme 9. Self-assembly of palladium–diphosphine capsules **1A·2** and **1B·2** by the use of a) precharged and b) neutral building blocks (schematic picture).

plexes **1A** or **1B**, respectively: $\Delta\delta(CH_2CH_3)_2 = 0.33–0.37$, $\Delta\delta(CH_2CH_3)_2 = 0.16–0.23$, $\Delta\delta(CH_2N) = 0.06–0.12$, and $\Delta\delta(NCH_3) = 0.07–0.13$ ppm (Figures 10 and 11). The upfield shifts point to partial inclusion of the diethylammonium-

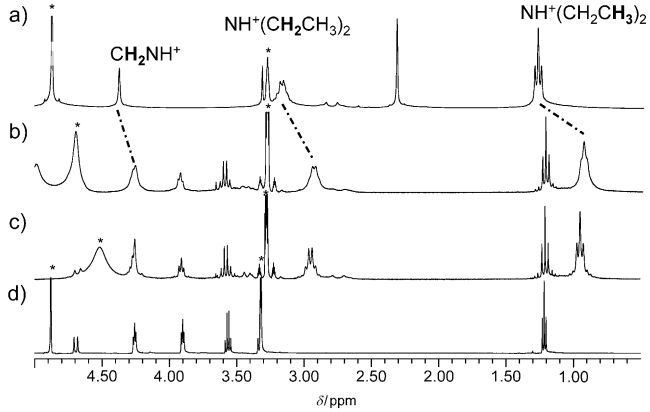


Figure 10. ^{1}H NMR spectra of palladium capsule **1(A)·2** self-assembled from neutral building blocks: a) **1(A-HOTs)** in CD_3OD at 20 °C; b) capsule **1(A)·2** in CD_3OD/D_2O (90:10 v/v) at 20 °C, [**1A**] = [**2**] = 2 mM; c) capsule **1(A)·2** at 40 °C; and d) **2-SO$_3$Na** in CD_3OD at 20 °C. Asterisks indicate solvent signals.

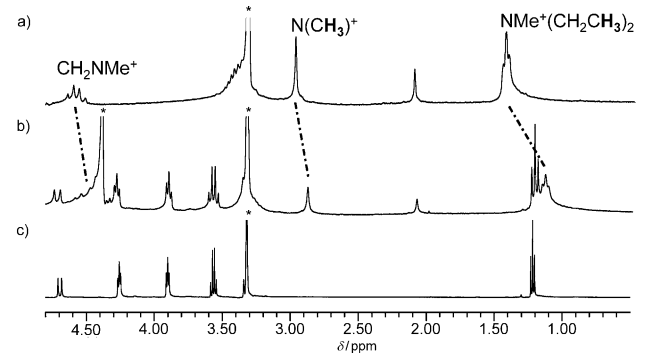


Figure 11. ^{1}H NMR spectra of palladium capsule **1(B-MeOTf)·2** self-assembled from precharged building blocks in CD_3OD: a) **1(B-MeOTf)** at 20 °C; b) capsule **1(B-MeOTf)·2** at 60 °C, [**1B**] = 2 mM, [**2**] = 4 mM; and c) **2-SO$_3$Na** at 20 °C. Asterisks indicate solvent signals.

methyl substituents inside the hydrophobic cavity of the capsule. The observed upfield shifts of the palladium capsules **1A·2** and **1B·2** are smaller than those of the diphosphine capsules **A·2** and **B·2** and of the previously reported palladium capsule [Pd(*trans*-**C**)(*p*-C_6H_4-CN)(Br)]**·2** ($\Delta\delta(CH_2CH_3) = 0.58$, $\Delta\delta(CH_2CH_3) = 0.39$, $\Delta\delta(CH_2N) = 0.17$ ppm).[5] Even though the size of $\Delta\delta$ depends on the exact nature of the metal complex, our observations indicate that the conformational rigid *cis*-$PdCl_2$ complexes **1A** and **1B** experience less side-chain encapsulation and fit less well onto calix[4]arene than the corresponding free ligands. In addition, because the capsule is also occupied by the palladium dichloride species, less space is available to accommodate side chains.

A single set of proton resonances for the free and bound building blocks was observed in the temperature window 0–60 °C for all the ionic-based palladium capsules. Variable-temperature ^{1}H NMR spectra of the palladium capsules show line broadening at 20 °C, in particular for the palladium building blocks, and sharper resonances at higher temperatures (40 and 60 °C; Figure 10).[16b] The observed line broadening indicates that the phosphorus substituents of the rigid palladium complex are not equivalent anymore upon capsule formation because they experience different environments. At higher temperatures, the exchange process between the free and bound building blocks and the bond-rotation rates are faster, thereby resulting in sharper NMR spectra. The phosphorus chemical shifts of **1A** and **1B** in their capsular form **1A·2** and **1B·2** did not exhibit a noteworthy shift compared to the monomeric form ($\Delta\delta \leq 0.8$ ppm), thus indicating that the *cis* geometry around the phosphorus atoms did not change.[24] Additional support for the formation of the palladium capsules **1A·2** and **1B·2** comes from Job's plot analysis of titration experiments carried out in CD_3OD at 60 °C (at 20 °C, the proton signals were too broad to be accurately determined). The observed maximum at a mole fraction of 0.5 proves the 1:1 stoichiometry between **1(A-MeOTf)** and **2-SO$_3$Na**, and between **1(B-MeOTf)** and **2-SO$_3$Na** (Figure 12).

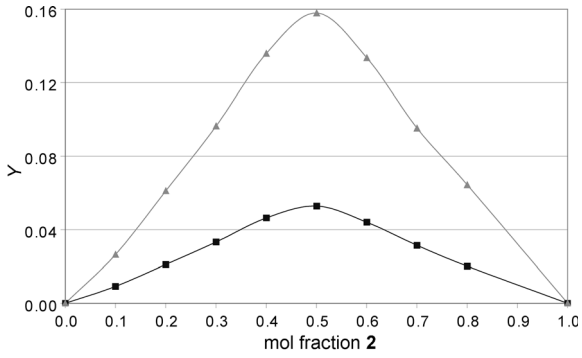


Figure 12. Job plot for **1(A-MeOTf)** with calix **2-SO$_3$Na** ($Y = (\Delta\delta_{1A}) \times$ (mol fraction **1A**)) in CD_3OD at 60 °C. Data points represent the absolute upfield shifts ($\Delta\delta_{1A}$) of $CH_2NH^+(CH_2CH_3)_2$ protons of **1A·2** relative to the chemical shifts of free **1A**: (▲) CH_2CH_3, (■) CH_2CH_3.

Just like the guanidinium-based capsule **E·2**, NMR spectroscopic studies show that addition of cesium carbonate (20 equiv) to a solution of the palladium capsule **1(A-MeOTf)·2** in methanol results in precipitation of calix[4]arene **2**, whereas the N-methylated palladium complex **1(A-MeOTf)** remains intact. Upon addition of *p*-toluenesulfonic acid (20 equiv) to **1(A-MeOTf)·2** no precipitation appears, but, judging from the NMR spectroscopic studies, the presence of an acid destabilizes the ionic-based capsule: $\Delta\delta$ of $N(CH_2CH_3)_2^+$ decreased from 0.35 to 0.09 ppm at 60 °C.

The ESI-MS spectra confirm the formation of the palladium capsules **1A·2** and **1B·2**. Prominent doubly and triply charged ion peaks are observed for the capsules in CH_3OH

at *m/z* 957.30 for $[\mathbf{1(A)\cdot 2}-\mathrm{Cl}+\mathrm{H}]^{2+}$, at *m/z* 652.60 for $[\mathbf{1(A\text{-}MeOTf)\cdot 2}\text{-}2\,\mathrm{Cl}+\mathrm{Na}]^{3+}$, at *m/z* 1023.37 for $[\mathbf{1(B)\cdot 2}-2\,\mathrm{Cl}]^{2+}$, and at *m/z* 701.28 for $[\mathbf{1(B\text{-}MeOTf)\cdot 2}-2\,\mathrm{Cl}+\mathrm{H}]^{3+}$ (Figures 13 and 14). The charge on the capsules is created by the loss of one or two chloride ligands from the palladium complex and/or by addition of protons or sodium cations from the solution. All the ion peaks of the capsule correspond to 1:1 complexes, and no ion peaks for higher aggregates were detected. Comparison of the measured isotope patterns of the capsules with the calculated ones confirms the elemental composition and charge state. The palladium dichloride complexes contain a tetracationic diphosphine and four triflate counterions. Interestingly, the ESI-MS spectra of the palladium complexes show that one to three out of their four triflate counterions remain attached to the ammonium groups during the ionization process. Examples are ion peaks at *m/z* 694.21 for $[\mathbf{1(A\text{-}MeOTf)}-\mathrm{Cl}-\mathrm{OTf}]^{2+}$ and at *m/z* 778.22 for $[\mathbf{1(B\text{-}MeOTf)}-\mathrm{Cl}-\mathrm{OTf}]^{2+}$. None of the ion peaks of the palladium capsules contains counterions,

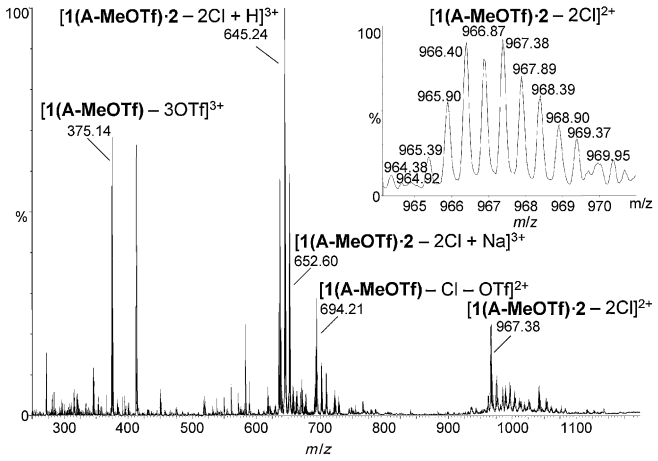


Figure 13. ESI-MS spectrum of a palladium capsule **1(A-MeOTf)·2** self-assembled of precharged building blocks (insets: measured isotope patterns).

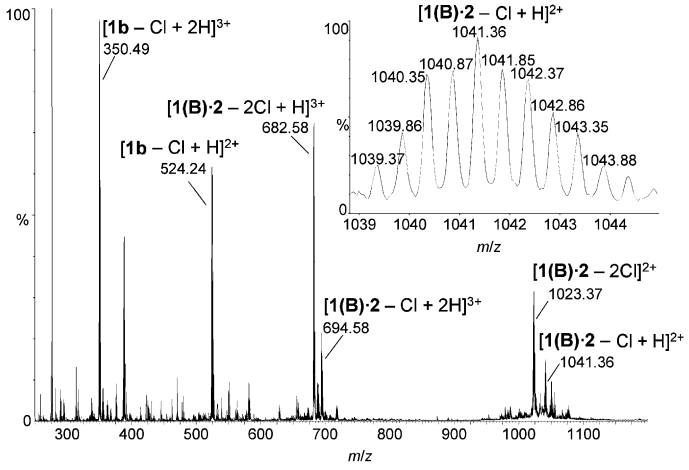


Figure 14. ESI-MS spectrum of a palladium capsule **1(B)·2** self-assembled of neutral building blocks (insets: measured isotope patterns).

thereby indicating that the palladium capsules do not encapsulate counterions. The absence of the counterions also indicates that the palladium complexes prefer to associate with one calix[4]arene rather than with one to three triflate counterions.[13]

Structure

After characterizing the metallodiphosphine capsules **1A·2** and **1B·2**, we studied their capsular structures by molecular modeling (PM3 level). The modeled structures of the d^8 palladium complexes **1A** and **1B**, which contain the dppe- and DPEphos-type ligands, show that they both adopt a square-planar geometry with the diphosphine ligand chelated in a *cis* fashion (Scheme 10). The four aryl groups of **1A** point in a slightly more uniform direction than the aryl groups of **1B**, that is, they are better preorganized for capsule formation. The reported X-ray structures of related [Pd(dppe)] and [Pd(DPEphos)] complexes illustrate that the relative spatial arrangement of the four aryl groups and the diphenyl ether backbone can vary to some extent.[10a,17b,22,25a,b] The resemblance between the modeled structure and the related X-ray structures is better for **1A** than for **1B**. The palladium complexes **1A** and **1B** might be rigid compared to their corresponding free ligands, but they can still rotate around some bonds, that is, around the Pd–P, P–Ar, and Ar–CH_2 bonds, and around the diphenyl ether backbone (Figure 15).

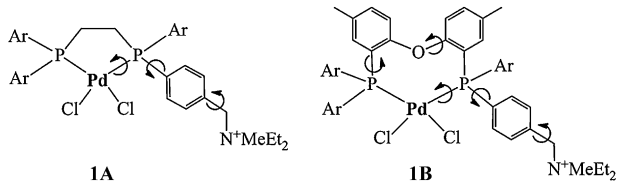
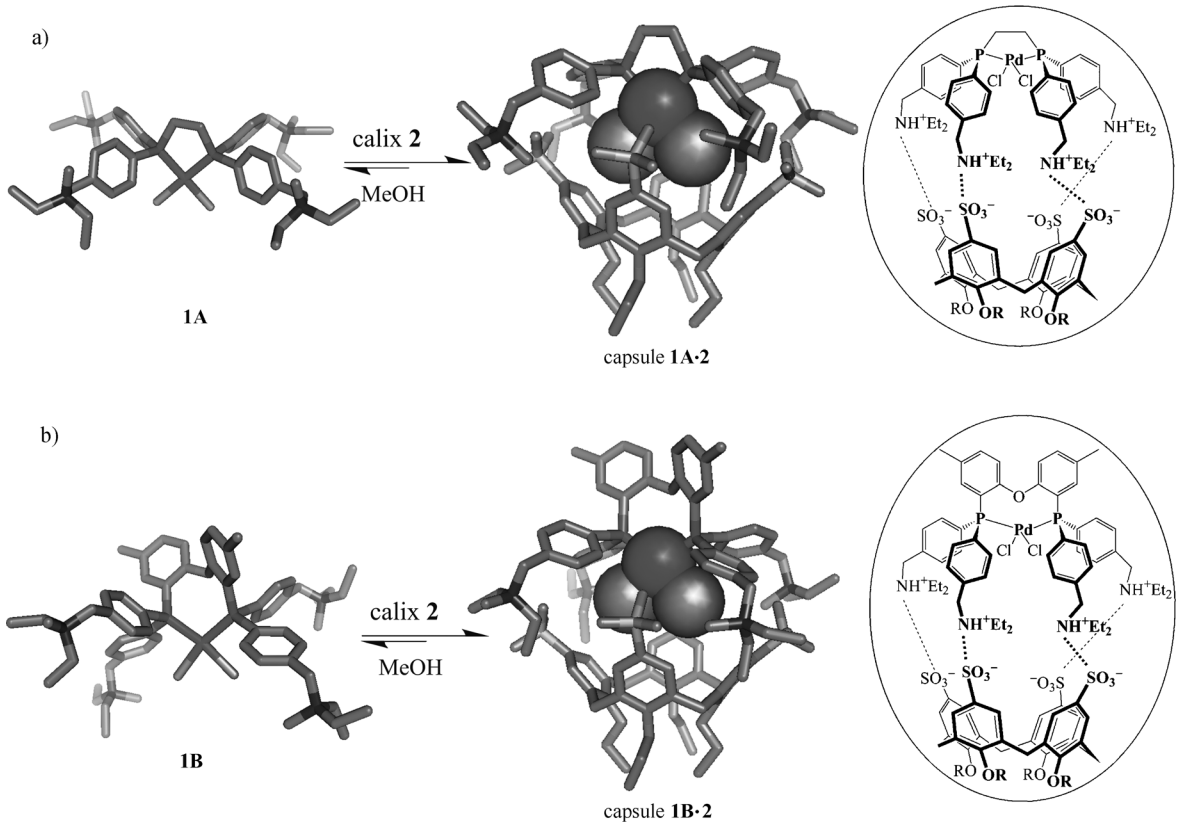


Figure 15. Possible bond rotations in the Pd complexes **1A** and **1B**.

In this way, they can adopt the proper conformation needed for capsule self-assembly. We assume that the transition-metal complexes will adopt higher-energy conformations only if the energy gain achieved upon capsule formation will compensate the energy loss. The modeled structures of the palladium capsules **1A·2** and **1B·2** illustrate that the capsules have a proper capsular structure with the two chloride ligands pointing into the interior of the capsule. Noteworthy, the calculated bite angles (P–Pd–P) of **1A** and **1B** are comparable to the literature values and do not change significantly upon capsule formation (Table 2).

Conclusion

We have demonstrated that the scope of capsules based on functionalized diphosphine ligands or metal complexes thereof can easily be extended. These capsules are formed by ionic interactions and are composed of a tetracationic diphosphine ligand and a complementary tetraanionic calix[4]arene. Encapsulation of a transition metal within the capsu-



Scheme 10. Self-assembly of metallodiphosphine capsules a) **1A·2** and b) **1B·2**: modeled and molecular structures.

Table 2. Bite angles (P–Pd–P) for the Pd complexes **1A** and **1B**, the Pd capsules **1A·2** and **1B·2**, and related Pd complexes.

	P–Pd–P		P–Pd–P
1A	86° (calcd)	**1B**	107° (calcd)
1A·2	86° (calcd)	**1B·2**	111° (calcd)
[Pd(dppe)Cl_2][25a]	86° (X-ray)	[Pd(DPEphos)Cl_2][25c]	101° (X-ray)
[Pd(dppe)][25c]	85° (70–95°)	[Pd(DPEphos)Cl_2][25c]	102° (86–120°)
(flexibility range)	(calcd)	(flexibility range)	(calcd)

les is achieved successfully by self-assembly of a transition-metal complex that contains a tetracationic ligand and a tetraanionic calix[4]arene. Diphosphine ligands with different flexibilities and shapes (i.e., different backbones and cationic binding motifs) assembled into (metallo)capsules with the proper capsular structure, as is indicated by ^{1}H NMR spectroscopy, 1D NOESY, ESI-MS, and modeling studies. This approach to metal encapsulation opens up new opportunities to control the activity, stability, and selectivity of the potential homogeneous catalysts.

Experimental Section

General Remarks

All reactions were carried out under a dry, inert atmosphere of purified nitrogen or argon using standard Schlenk techniques unless stated otherwise. Solvents were dried and distilled under nitrogen prior to use. Diethyl ether, THF, hexanes, and pentane were distilled from sodium/benzophenone. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) was distilled from sodium. Dichloromethane, methanol, and acetonitrile were distilled from CaH_2. Deuterated solvents were distilled from the appropriate drying agents. Unless stated otherwise, all chemicals were obtained from commercial suppliers and used as received. Bis(*N,N*-diethylamino)chlorophosphine,[26] (4-bromobenzyl)diethylamine,[11] and 5,11,17,23-tetrakis(sulfonato)-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene tetrasodium salt **2-SO_3Na**[4b] were synthesized according to reported procedures. NMR spectra were recorded with Varian Inova 500, Bruker Avance DRX 300, and Varian Mercury 300 NMR spectrometers. Chemical shifts are given relative to TMS (^{1}H and ^{13}C NMR spectroscopy), 85% H_3PO_4 (^{31}P NMR spectroscopy), and Cl_3CF (^{19}F NMR spectroscopy). Chemical shifts are given in ppm. 1D NOESY measurements (1D transient NOE) were carried out with a double-pulsed field-gradient spin echo (DPFGSE) excitation. Elemental analyses were performed at the H. Kolbe Mikroanalytisches laboratory in Mülheim (Germany). High-resolution fast atom bombardment mass spectrometry (HRMS FAB) measurements were carried out with a JEOL JMS SX/SX 102A at the Department of Mass Spectrometry at the University of Amsterdam. Electrospray ionization mass spectrometry (ESI-MS) measurements were carried out with a Q-TOF (Micromass, Waters, Whyttenshawe, UK) mass spectrometer equipped with a Z-spray orthogonal nanoelectrospray source, using Econo Tips (New Objective, Woburn, MA) to create an offline nanospray, at the Department of Mass Spectrometry of Biomacromolecules at the University of Amsterdam. Molecular modeling calculations were performed with Spartan 04V1.0.3 software on the semiempirical PM3 level. Abbreviations used: Me-*p*-$C_6H_4SO_3^-$ = OTs^-, $CF_3SO_3^-$ = OTf^-, and cod = 1,5-cyclooctadiene. The [$PdCl_2$(**b**)] and [$PdCl_2$(**B**)] complexes that contain the DPEphos-type ligand give broad carbon resonances in their ^{13}C NMR spectra and therefore could not be characterized by carbon NMR spectroscopy.

*1,2-Bis(bis[p-[(diethylamino)methyl]phenyl]phosphino)ethane (**a**)*

n-Butyllithium (2.5 M in hexanes, 15.09 mL, 37.72 mmol) was added to THF (100 mL) at 0 °C, and the solution was further cooled to −65 °C. A yellow solution of (4-bromobenzyl)diethylamine (9.14 g, 37.72 mmol) in THF (40 mL) was added to the *n*-butyllithium solution in 1 h. The resulting pink reaction mixture was stirred for another 30 min at −45 °C. After cooling the resulting yellow reaction mixture to −65 °C, a solution of 1,2-bis(dichlorophosphino)ethane (1.99 g, 8.57 mmol) in THF (30 mL) was added in 30 min. The resulting green reaction mixture was allowed to warm to room temperature overnight. The yellow reaction mixture was hydrolyzed with degassed water (3 mL), and the solvent was removed in vacuo. Subsequently, the yellow viscous oil was dissolved in diethyl ether and washed with degassed water. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$, and the solvent was removed in vacuo. The resulting yellow viscous oil was purified by column chromatography (silica gel, 95–65 % petroleum ether (PE) 40/60, 0–30 % EtOAc, 5 % NEt_3). Product **a** was obtained as a white solid (3.80 g, 5.14 mmol, 60 %). ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): $\delta = 7.25$ (s, 16H; PC_6H_4), 3.52 (s, 8H; CH_2N), 2.48 (q, $J = 7.0$ Hz, 16H; CH_2CH_3), 2.02 (t, $J = 3.8$ Hz, 4H; CH_2CH_2), 1.01 ppm (t, $J = 7.1$ Hz, 24H; CH_2CH_3); ^{13}C{^{1}H} NMR (76 MHz, $CDCl_3$, 293 K): $\delta = 141.1$ (s; Cq, PC_6H_4), 136.6 (s; Cq, PC_6H_4), 133.0 (s; CH, PC_6H_4), 129.3 (s; CH, PC_6H_4), 57.6 (s; CH_2N), 47.1 (s; CH_2CH_3), 24.4 (s; CH_2CH_2), 12.1 ppm (s; CH_2CH_3); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 293 K): $\delta = -12.7$ ppm (s); HRMS (FAB+): *m*/*z* calcd for $[C_{46}H_{68}N_4P_2+H]^+$: 739.4998; found: 739.4990.

2,2′-[Bis(bis-diethylamino)phosphonito]-4,4′-dimethyldiphenyl ether[10]

A solution of *p*-tolyl ether (5.10 g, 25.72 mmol) and TMEDA (8.54 mL 56.59 mmol) in hexanes (20 mL) was stirred and cooled to −45 °C, thereby giving a white suspension. Subsequently *n*-butyllithium (2.5 M in hexanes, 22.64 mL, 56.59 mmol) was added dropwise and the reaction mixture was allowed to warm to room temperature overnight, which resulted in a yellow suspension. The dilithio salt was isolated from excess amounts of *n*-butyllithium by leaving the salt to precipitate at −20 °C for 7 h and subsequently removing the orange supernatant liquid with a syringe (this step is not necessary). Subsequently, a solution of bis(diethylamino)chlorophosphine (11.38 g, 54.01 mmol) in hexanes/diethyl ether (40 mL, 1:1) was stirred and cooled to −78 °C. The off-white dilithio salt was dissolved in diethyl ether (40 mL) and was slowly added to the solution of $ClP(NEt_2)_2$ with a Teflon cannula. The reaction mixture was allowed to warm to room temperature overnight. The salts were filtered off from the yellow solution and washed twice with diethyl ether. Evaporation of the solvents in vacuo yielded 2,2′-[bis(bis-diethylamino)phosphonito]-4,4′-dimethyldiphenyl ether as a yellow oil. ^{31}P{^{1}H} NMR (121.5 MHz, 293 K): $\delta = 93.53$ ppm (s).

2,2′-Bis(dichlorophosphino)-4,4′-dimethyldiphenyl ether[10]

A solution of 2,2′-[bis(bis-diethylamino)phosphonito]-4,4′-dimethyldiphenyl ether in hexanes (600 mL) was stirred and cooled down to −78 °C. HCl gas was bubbled into the reaction mixture over 1.5 h, which resulted immediately in large amounts of white precipitation. Subsequently, the reaction mixture was allowed to warm to room temperature. The salts were filtered off and washed with diethyl ether (100 mL). Evaporation of the solvents resulted in a white powder. Crystallization from hexanes (35 mL) at −20 °C yielded 2,2′-bis(dichlorophosphino)-4,4′-dimethyldiphenyl ether as an off-white powder (52 %, 5.34 g, 13.35 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): $\delta = 7.85$ (brs, 2H; H_{Ar}), 7.30 (dd, $J =$ 1.5 Hz, $J = 8.5$ Hz, 2H; H_{Ar}), 6.81 (dt, $J = 3.0$ Hz, $J = 8.5$ Hz, 2H; H_{Ar}), 2.44 ppm (s, 6H; CH_3); ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, 293 K): $\delta =$ 159.12 ppm (s).

*2,2′-Bis(bis[p-[(diethylamino)methyl]phenyl}phosphino)-4,4′-dimethyldiphenyl ether (**b**)*

n-Butyllithium (2.5 M in hexanes, 11.39 mL, 24.47 mmol) was added to THF (75 mL) at 0 °C, and the solution was further cooled to −65 °C. A yellow solution of (4-bromobenzyl)diethylamine (6.89 g, 28.47 mmol) in THF (30 mL) was added to the *n*-butyllithium solution in 1 h. The resulting pink reaction mixture was stirred for another 30 min at −45 °C. After cooling the resulting pale orange reaction mixture to −65 °C, a solution of 2,2′-bis(dichlorophosphino)-4,4′-dimethyldiphenyl ether (2.28 g, 5.69 mmol) in THF (20 mL) was added in 30 min. The resulting green reaction mixture was allowed to warm to room temperature overnight. The orange reaction mixture was hydrolyzed with degassed water (3 mL), and the solvent was removed in vacuo. Subsequently, the yellow viscous oil was dissolved in diethyl ether and washed with degassed water. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$, and the solvent was removed in vacuo. The resulting yellow viscous oil was purified by column chromatography (silica gel, 97–45 % hexanes, 0–50 % EtOAc, 3–5 % NEt_3). Product **b** was obtained as a white solid (3.12 g, 3.43 mmol, 60 %). ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): $\delta = 7.19$ (d, $J =$ 7.6 Hz, 8H; PC_6H_4), 7.18–7.07 (m, 8H; PC_6H_4), 6.87 (d, $J = 8.1$ Hz, 2H; OC_6H_3), 6.56 (brs, 2H; OC_6H_3), 6.44–6.40 (m, 2H; OC_6H_3), 3.51 (s, 8H; CH_2N), 2.47 (q, $J = 6.9$ Hz, 16H; CH_2CH_3), 2.09 (s, 6H; CH_3), 0.99 ppm (t, $J = 7.2$ Hz, 24H; CH_2CH_3); ^{13}C{^{1}H} NMR (76 MHz, $CDCl_3$, 293 K): $\delta = 157.8$ (brs; Cq, C_{Ar}), 140.5 (s; Cq, C_{Ar}), 135.5 (s; Cq, C_{Ar}), 134.6 (s; Cq, C_{Ar}), 134.3 (s; CH, OC_6H_3), 134.0 (s; CH, PC_6H_4), 132.8 (s; Cq, C_{Ar}), 131.0 (s; CH, OC_6H_3), 129.2 (s; CH, PC_6H_4), 118.1 (s; CH, OC_6H_3), 57.7 (s; CH_2N), 47.1 (s; CH_2CH_3), 21.2 (s; CH_3), 12.2 ppm (s; CH_2CH_3); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 293 K): $\delta = -16.4$ (s); HRMS (FAB+): *m*/*z* calcd for $[C_{58}H_{76}ON_4P_2+H]^+$: 907.5573; found: 907.5588; elemental analysis calcd (%) for $C_{58}H_{76}N_4OP_2$: C 76.79, H 8.44, N 6.18; found: C 76.67, H 8.40, N 6.11.

4,5-Bis(diethoxyphosphonito)-9,9-dimethylxanthene[12]

A yellow solution of 9,9-dimethylxanthene (10.17 g, 48.36 mmol) and TMEDA (21.89 mL, 145.08 mmol) in diethyl ether (120 mL) was cooled to 0 °C. Next, *n*-butyllithium (2.5 M in hexanes, 46.43 mL, 116.06 mmol) was added dropwise, and the reaction mixture was stirred overnight. The resulting dark red solution was cooled to −78 °C, and a solution of diethyl chlorophosphite (18.07 mL, 125.74 mmol) in diethyl ether (120 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The solvent was evaporated in vacuo to give a yellow oil. The salts were extracted by adding dichloromethane (100 mL) and degassed water (100 mL) to the crude product. After vigorous stirring, the organic layer was washed twice with degassed water and dried over $MgSO_4$. Evaporation of the solvent resulted in 4,5-bis(diethoxyphosphino)-9,9-dimethylxanthene as a yellow sticky oil (21.13 g, 46.91 mmol, 97 %). ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): $\delta = 7.60$ (d, $J = 7.4$ Hz, 2H; H_3), 7.43 (d, $J = 7.6$ Hz, 2H; H_1), 7.11 (t, $J = 7.4$ Hz, 2H; H_2), 3.94 (dm, 8H; OCH_2CH_3), 1.59 (s, 6H; $C(CH_3)_2$), 1.25 ppm (t, $J = 7.1$ Hz, 12H; OCH_2CH_3); ^{13}C{^{1}H} NMR (76 MHz, $CDCl_3$, 293 K): $\delta =$ 152.4 (brt; C^{4a}), 130.1 (s; Cq, C_{Ar}), 129.1 (s; CH, C_{Ar}), 128.7 (s; Cq, C_{Ar}), 128.2 (s; CH, C_{Ar}), 123.4 (s; CH, C_{Ar}), 63.3 (s; CH_2CH_3), 34.4 (s; $C(CH_3)_2$), 32.6 (s; $C(CH_3)_2$), 17.7 ppm (s; CH_2CH_3); ^{31}P{^{1}H} NMR (122 MHz, $CDCl_3$, 293 K): $\delta = 149.5$ ppm (s).

*4,5-Bis(bis[p-[(diethylamino)methyl]phenyl}phosphino)-9,9-dimethylxanthene (**c**)*

n-Butyllithium (2.5 M in hexanes, 12.88 mL, 32.20 mmol) was added to THF (100 mL) at 0 °C, and the solution was further cooled to −65 °C. A yellow solution of (4-bromobenzyl)diethylamine (7.80 g, 32.20 mmol) in THF (35 mL) was added to the *n*-butyllithium solution in 1 h. The resulting pink reaction mixture was stirred for another 30 min at −45 °C. After cooling the resulting orange reaction mixture to −65 °C, a solution of 4,5-bis(diethoxyphosphino)-9,9-dimethylxanthene (2.90 g, 6.44 mmol) in THF (25 mL) was added in 30 min. The resulting green reaction mixture was allowed to warm to room temperature overnight. The pale orange reaction mixture was hydrolyzed with degassed water (3 mL), and the solvent was removed in vacuo. Subsequently, the yellow viscous oil was dissolved in diethyl ether and washed with degassed water. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$, and the solvent was removed in vacuo. The resulting dark-orange viscous oil was purified by column chromatography (silica gel, 97–67 % hexanes, 0–30 % EtOAc, 3 % NEt_3). The product **c** was obtained as a white solid (3.02 g,

3.25 mmol, 51%). ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ=7.34 (d, J=7.8 Hz, 2H; H_3), 7.17 (d, J=7.8 Hz, 8H; PC_6H_4), 7.16–7.08 (m, 8H; PC_6H_4), 6.90 (t, J=7.6 Hz, 2H; H_2), 6.52 (d, J=7.6 Hz, 2H; H_1), 3.51 (s, 8H; CH_2N), 2.49 (q, J=7.1 Hz, 16H; CH_2CH_3), 1.61 (s, 6H; $C(CH_3)_2$), 1.01 ppm (t, J=7.1 Hz, 24H; CH_2CH_3); ^{13}C{^{1}H} NMR (76 MHz, $CDCl_3$, 293 K): δ=152.6 (brt; C^{4a}), 140.3 (s; Cq, C_{Ar}), 136.1 (s; Cq, C_{Ar}), 134.3 (s; CH, PC_6H_4), 132.4 (s; C_1), 130.1 (s; Cq, C_{Ar}), 129.1 (s; CH, PC_6H_4), 126.6 (s; C_3), 123.5 (s; C_2), 57.7 (s; CH_2N), 47.1 (s; CH_2CH_3), 34.8 (s; $C(CH_3)_2$), 32.5 (s; $C(CH_3)_2$), 12.1 ppm (s; CH_2CH_3); ^{31}P{^{1}H} NMR (122 MHz, $CDCl_3$, 293 K): δ=−18.3 ppm (s); HRMS (FAB+): m/z calcd for $[C_{59}H_{76}ON_4P_2Cl_4+H]^+$: 919.5573; found: 919.5574; elemental analysis calcd (%) for $C_{59}H_{76}N_4OP_2$: C 77.09, H 8.33, N 6.10; found: C 76.88, H 8.39, N 5.96.

*1,2-Bis(bis{p-[(diethylammonium chloride)methyl]phenyl}phosphino)ethane (**A-HCl**)*

A 2M solution of HCl in diethyl ether (0.50 mL, 1.00 mmol) was added dropwise to a solution of **a** (85 mg, 114 μmol) in diethyl ether (10 mL), upon which a white precipitation appeared. After stirring for 30 min, the volatiles were removed in vacuo and **A-HCl** was obtained as a white powder in quantitative yield. ^{1}H NMR (300 MHz, CD_3OD, 293 K): δ=7.64 (d, J=7.9 Hz, 8H; PC_6H_4), 7.46 (m, 8H; PC_6H_4), 4.40 (s, 8H; CH_2N), 3.31–3.15 (m, 16H; CH_2CH_3), 2.18 (t, J=4.3 Hz, 4H; CH_2CH_2), 1.38 ppm (t, J=7.3 Hz, 24H; CH_2CH_3); ^{13}C{^{1}H} NMR (75 MHz, CD_3OD, 293 K): δ=139.5 (brs; Cq, PC_6H_4), 133.2 (t, J=9.3 Hz; CH, PC_6H_4), 131.1 (t, J=3.3 Hz; CH, PC_6H_4), 130.7 (s; Cq, PC_6H_4), 55.3 (s; CH_2N), 46.7 (s; CH_2CH_3), 46.6 (s; CH_2CH_3), 23.0 (brs; CH_2CH_2), 7.7 ppm (s; CH_2CH_3); ^{31}P{^{1}H} NMR (121.5 MHz, CD_3OD, 293 K): δ=−12.7 ppm (s); HRMS (FAB+): m/z calcd for $[C_{46}H_{72}N_4P_2Cl_4-2H-3Cl]^+$: 775.4764; found: 775.4777.

*2,2′-Bis(bis{p-[(diethylammonium chloride)methyl]phenyl}phosphino)-4,4′-dimethyldiphenyl ether (**B-HCl**)*

This compound was prepared similarly to **A-HCl**, starting from **b**. ^{1}H NMR (300 MHz, CD_3OD, 293 K): δ=7.62 (d, J=7.3 Hz, 8H; PC_6H_4), 7.37–7.22 (m, 8H; PC_6H_4), 7.11 (d, J=7.9 Hz, 2H; OC_6H_3), 6.66 (d, J=4.3 Hz, 2H; OC_6H_3), 6.56–6.50 (m, 2H; OC_6H_3), 4.41 (s, 8H; CH_2N), 3.31–3.12 (m, 16H; CH_2CH_3), 2.16 (s, 6H; CH_3), 1.37 ppm (brt, 24H; CH_2CH_3); ^{13}C{^{1}H} NMR (75 MHz, CD_3OD, 293 K): δ=156.9 (brs; Cq, C_{Ar}), 138.5 (brs; Cq, C_{Ar}), 134.4 (s; CH, C_{Ar}), 134.1 (s; CH, C_{Ar}), 133.1 (s; Cq, C_{Ar}), 131.4 (s; Cq, C_{Ar}), 130.9 (brs; CH, C_{Ar}), 130.4 (s; CH, C_{Ar}), 126.6 (brs; Cq, C_{Ar}), 117.7 (s; CH, C_{Ar}), 55.4 (s; CH_2N), 46.7 (s; CH_2CH_3), 46.6 (s; CH_2CH_3), 19.4 (s; CH_3), 7.7 ppm (brs; CH_2CH_3); ^{31}P{^{1}H} NMR (121.5 MHz, CD_3OD, 293 K): δ=−15.3 ppm (s); HRMS (FAB+): m/z calcd for $[C_{58}H_{80}ON_4P_2Cl_4-2H-3Cl]^+$: 943.5339; found: 943.5336.

*4,5-Bis(bis{p-[(diethylammonium chloride)methyl]phenyl}phosphino)-9,9-dimethylxanthene (**C-HCl**)*

This compound was prepared similarly to **A-HCl**, starting from **c**. ^{1}H NMR (500 MHz, CD_3OD, 293 K): δ=7.59 (d, J=8.1 Hz, 10H; H_3 + PC_6H_4), 7.33–7.30 (m, 8H; PC_6H_4), 7.03 (t, J=7.7 Hz, 2H; H_2), 6.48 (d, J=7.6 Hz, 2H; H_1), 4.40 (s, 8H; CH_2N), 3.29–3.19 (m, 16H; CH_2CH_3), 1.68 (s, 6H; CCH_3), 1.38 ppm (dt, J=3.0 and 7.5 Hz, 24H; CH_2CH_3); ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): δ=12.12 ppm (s, 4H; NH^+); ^{13}C{^{1}H} NMR (126 MHz, CD_3OD, 293 K): δ=153.2 (t, J=9.6 Hz; CO), 140.6 (t, J=7.2 Hz), 136.0 (t, J=10.9 Hz), 132.8 (s; C_1), 132.4 (t; J=3.2 Hz), 131.9 (s), 131.6 (s), 129.0 (s), 125.4 (t, J=8.9 Hz), 125.2 (s; C_2), 57.0 (s; CH_2N), 48.3 (s; CH_2CH_3), 48.2 (s; CH_2CH_3), 35.7 (s; CCH_3), 32.7 (s; CCH_3), 9.3 (s; CH_2CH_3), 9.2 ppm (s; CH_2CH_3); ^{31}P{^{1}H} NMR (202 MHz, CD_3OD, 293 K): δ=−16.8 ppm (s); ^{31}P{^{1}H} NMR (202 MHz, [D$_6$]DMSO, 293 K): δ=−17.8 ppm (s); HRMS (FAB+): m/z calcd for $[C_{59}H_{80}ON_4P_2Cl_4-4Cl-3H]^+$: 919.5573; found: 919.5573.

2,7-Di-tert-butyl-4,5-bis[bis(diethylamino)phosphonito]-9,9-dimethylxanthene[17b]

A solution of *n*-butyllithium (2.5M in hexanes, 27.48 mL, 68.71 mmol) was added dropwise to a solution of 2,7-di-*tert*-butyl-4,5-dibromo-9,9-dimethylxanthene (16.50 g, 34.35 mmol) in THF (250 mL) at −70°C. After stirring the pink suspension for 2 h at −70°C, a solution of bis(diethylamino)chlorophosphine (14.48 mL, 68.71 mmol) in THF (40 mL) was added dropwise at −70°C. The reaction mixture was allowed to warm to room temperature overnight, which resulted in a clear yellow solution. The solvents were removed in vacuo, and the residue was dissolved in hexanes (80 mL). The precipitated salts were removed from the solution by filtration. Evaporation of the solvents in vacuo yielded 2,7-di-*tert*-butyl-4,5-bis[bis(diethylamino)phosphonito]-9,9-dimethylxanthene as a yellow powder (22.87 g, 34.09 mmol, 99%). ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ=7.33 (brs, 2H; PC_6H_2), 7.26 (brs, 2H; PC_6H_2), 3.15–2.93 (m, 16H; CH_2CH_3), 1.57 (s, 6H; $C(CH_3)_2$), 1.31 (s, 18H; $C(CH_3)_3$), 0.99 ppm (t, J=6.9 Hz, 24H; CH_2CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 293 K): δ=149.0 (brs; Cq, C_{Ar}), 144.1 (s; Cq, C_{Ar}), 129.4 (s; Cq, C_{Ar}), 128.8 (s; Cq, C_{Ar}), 127.4 (s; CH, C_{Ar}), 122.6 (s; CH, C_{Ar}), 43.4 (brs; NCH_2CH_3), 34.9 (s; $C(CH_3)_3$), 34.7 (s; $C(CH_3)_2$), 33.4 (s; $C(CH_3)_3$), 32.0 (s; $C(CH_3)_2$), 14.9 ppm (s; NCH_2CH_3); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 293 K): δ=93.1 ppm (s).

2,7-Di-tert-butyl-4,5-bis(dichlorophosphino)-9,9-dimethylxanthene[17b]

A solution of distilled phosphorus trichloride (29.97 mL, 343.5 mmol) in diethyl ether (100 mL) was added to a solution of 2,7-di-*tert*-butyl-4,5-bis-[bis(diethylamino)phosphonito]-9,9-dimethylxanthene (22.87 g, 34.09 mmol, 99%) in diethyl ether (200 mL) at 0°C. The reaction mixture was allowed to warm to room temperature overnight. Next, the reaction mixture was heated at reflux (50°C) for 20 h. After cooling to room temperature, the solvents were evaporated in vacuo, and the product was crystallized from hexanes (120 mL) at −20°C. After the solvents were removed and the product was dried in vacuo, 2,7-di-*tert*-butyl-4,5-bis(dichlorophosphino)-9,9-dimethylxanthene was obtained as an off-white powder (12.70 g, 24.23 mmol, 70%). ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ=7.90 (brs, 2H; PC_6H_2), 7.58 (brs, 2H; PC_6H_2), 1.66 (s, 6H; $C(CH_3)_2$), 1.36 ppm (s, 18H; $C(CH_3)_3$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 293 K): δ=149.0 (t, J=13.5; Cq, C_{Ar}), 147.7 (s; Cq, C_{Ar}), 129.9 (s; Cq, C_{Ar}), 128.1 (s; CH, C_{Ar}), 127.2 (s; Cq, C_{Ar}), 126.5 (s; CH, C_{Ar}), 35.6 (s; $C(CH_3)_3$), 35.0 (s; $C(CH_3)_2$), 32.8 (s; $C(CH_3)_3$), 31.9 ppm (s; $C(CH_3)_2$); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 293 K): δ=161.6 ppm (s).

*2,7-Di-tert-butyl-4,5-bis[bis(3-aminophenyl)phosphino]-9,9-dimethylxanthene (**d**)*

The solution of 2,7-di-*tert*-butyl-4,5-bis(dichlorophosphino)-9,9-dimethylxanthene (3.95 g, 7.57 mmol) in THF (60 mL) was added slowly to 1.0M THF solution of 3-[*N*,*N*-bis(trimethylsilyl)amino]phenylmagnesium chloride (37.83 mL, 37.83 mmol) at −25°C. The resulting yellow reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was hydrolyzed with degassed water (5 mL), and the solvent was removed in vacuo. Next, to receive the crude product as a powder, it was dissolved in dichloromethane, and the solvent was removed in vacuo. Subsequently, the product was extracted and *N*-deprotected by solid–liquid extraction with diethylamine (4×, 250 mL, 30 min, filtration over a glass filter (Por 4)). The product **d** was purified by column chromatography (basic alumina, dichloromethane/methanol, 95:5 then 80:20). The product was obtained as an orange powder (1.40 g, 1.86 mmol, 25%). ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ=7.31 (brs, 2H; PC_6H_2), 6.97 (t, J=7.3 Hz, 4H; PC_6H_4), 6.66 (brs, 2H; PC_6H_2), 6.64–6.49 (m, 12H; PC_6H_4), 3.52 (brs, 8H; NH_2), 1.62 (s, 6H; $C(CH_3)_2$), 1.10 ppm (s, 18H; $C(CH_3)_3$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 293 K): δ=151.2 (brt; Cq, C_{Ar}), 146.3 (t, J=4.1 Hz; Cq, C_{Ar}), 145.4 (s; Cq, C_{Ar}), 139.3 (t, J=6.2 Hz; Cq, C_{Ar}), 130.0 (s; CH, PC_6H_2), 129.9 (s; Cq, C_{Ar}), 129.2 (s; Cq, C_{Ar}), 129.0 (s; CH, PC_6H_4), 124.7 (t, J=8.8 Hz; CH, PC_6H_4), 123.2 (s; CH, PC_6H_2), 121.2 (t, J=11.0 Hz; CH, PC_6H_4), 115.5 (s, CH; PC_6H_4), 35.2 (s; $C(CH_3)_2$), 34.9 (s; $C(CH_3)_3$), 32.5 (s; $C(CH_3)_2$), 31.8 ppm (s; $C(CH_3)_3$); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 293 K): δ=−15.1 ppm (s); HRMS (FAB+): m/z calcd for $[C_{47}H_{52}ON_4P_2+H]^+$: 751.3695; found: 751.3678.

*2,7-Di-tert-butyl-4,5-bis{bis[(3-ammonium chloride)phenyl]phosphino}-9,9-dimethylxanthene (**D-HCl**)*

A 2 M solution of HCl in diethyl ether (3.20 mL, 6.40 mmol) was added dropwise to a solution of **d** (600.7 mg, 800.0 μmol) in dichloromethane (20 mL), upon which a fine pink precipitation appeared. After stirring for 30 min, the volatiles were removed in vacuo, and **D-HCl** was obtained as a pink powder in quantitative yield. ^{1}H NMR (300 MHz, CD_3OD, 293 K): δ = 7.60–7.47 (m, 6H; PC_6H_2+PC_6H_4), 7.41 (d, J = 7.4 Hz, 4H; PC_6H_4), 7.31 (brt, J = 7.3 Hz, 4H; PC_6H_4), 7.24 (s, 4H; PC_6H_4), 6.38 (s, 2H; PC_6H_2), 1.68 (s, 6H; $C(CH_3)_2$), 1.08 ppm (s, 18H; $C(CH_3)_3$); ^{13}C{^{1}H} NMR (75 MHz, CD_3OD, 293 K): δ = 146.4, 139.3, 134.5, 134.3, 131.1, 130.1, 129.3, 128.3, 127.7, 127.2, 124.8, 123.6, 34.5, 34.1, 31.7, 30.3 ppm; ^{31}P{^{1}H} NMR (121.5 MHz, CD_3OD, 293 K): δ = −13.7 ppm (s); HRMS (FAB+): m/z calcd for $[C_{47}H_{56}Cl_4N_4OP_2-3H-4Cl]^+$: 751.3695; found: 751.3687.

*2,7-Di-tert-butyl-4,5-bis{bis[(3-N,N-dimethylguanidinium chloride)phenyl]phosphino}-9,9-dimethylxanthene (**E-HCl**)*

An orange suspension of **D-HCl** (300 mg, 269 μmol) in degassed dimethylcyanamide (48.9 μL, 6.00 mmol) was heated at 110 °C for 24 h. Subsequently, the clear brown solution was cooled to room temperature, upon which a fine brown precipitation appeared. After washing the precipitation with diethyl ether (4×10 mL), the product **E-HCl** was obtained as an orange powder (314 mg, 267 μmol, 89 %). ^{1}H NMR (300 MHz, CD_3OD, 293 K): δ = 7.56 (d, J = 2.1 Hz, 2H; PC_6H_2), 7.47 (t, J = 7.8 Hz, 4H; PC_6H_4), 7.30 (d, J = 6.6 Hz, 4H; PC_6H_4), 7.20 (brt, 4H; PC_6H_4), 7.12 (brs, 4H; PC_6H_4), 6.60 (q, J = 2.4 Hz, 2H; PC_6H_2), 3.07 (s, 24H; $N(CH_3)_2$), 1.67 (s, 6H; $C(CH_3)_2$), 1.13 ppm (s, 18H; $C(CH_3)_3$); ^{13}C{^{1}H} NMR (75 MHz, CD_3OD, 293 K): δ = 155.9 (s; Cq, CN_3), 149.7 (brs; Cq, C_{Ar}), 146.1 (s; Cq, C_{Ar}), 138.8 (t, J = 7.0 Hz; Cq, C_{Ar}), 136.7 (t, J = 3.7 Hz; Cq, C_{Ar}), 132.1 (t, J = 10.7 Hz; CH, C_{Ar}), 129.7 (brs; CH, C_{Ar}), 129.4 (s; Cq, C_{Ar}), 129.0 (brt; CH, C_{Ar}), 128.7 (s; CH, C_{Ar}), 124.5 (s; CH, C_{Ar}), 124.1 (s; CH, C_{Ar}), 37.9 (s; NMe_2), 34.6 (s; $C(CH_3)_2$), 34.2 (s; $C(CH_3)_3$), 31.2 (s; $C(CH_3)_2$), 30.3 ppm (s; $C(CH_3)_3$); ^{31}P{^{1}H} NMR (121.5 MHz, CD_3OD, 293 K): δ = −14.5 ppm (s); HRMS (FAB+): m/z calcd for $[C_{59}H_{80}ON_{12}P_2Cl_4-3H-4Cl]^+$: 1031.5819; found: 1031.5829. three times with 20 mL pentane

*cis-[PdCl$_2$(**a**)] (**1a**)*

A solution of dppe-*p*-C_6H_4-CH_2NEt_2 **a** (0.915 g, 1.24 mmol) in dichloromethane (15 mL) was added to a solution of [(cod)$PdCl_2$] (0.354 g, 1.24 mmol) in dichloromethane (20 mL). The pale yellow reaction mixture was stirred for 1 h at room temperature. Subsequently, the solvent was evaporated and the precipitate was washed thoroughly with pentane (3×20 ml) and dried in vacuo. The product **1a** was obtained as a pale yellow powder (1.10 g, 1.20 mmol, 97 %). ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ = 7.83–7.71 (m, 8H; PC_6H_4), 7.42 (d, J = 8.0 Hz, 8H; PC_6H_4), 3.56 (s, 8H; CH_2N), 2.50 (q, J = 7.2 Hz, 16H; CH_2CH_3), 2.44–2.30 (m, 4H; CH_2CH_2), 1.01 ppm (t, J = 7.1 Hz, 24H; CH_2CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 293 K): δ = 145.6 (s; Cq, PC_6H_4), 133.9 (s; CH, PC_6H_4), 129.7 (s; CH, PC_6H_4), 126.2 (s; Cq, PC_6H_4), 57.7 (s; CH_2N), 47.4 (s; CH_2CH_3), 28.9 (brs; CH_2CH_2), 12.2 ppm (s; CH_2CH_3); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 293 K): δ = 64.4 ppm (s); HRMS (FAB+): m/z calcd for $[C_{46}H_{68}Cl_2N_4P_2Pd-Cl]^+$: 879.3656; found: 879.3637.

*cis-[PdCl$_2$(**b**)] (**1b**)*

This compound was prepared similarly to **1a**. The product was obtained as an orange powder (98 %). ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ = 7.54–7.41 (m, 8H; PC_6H_4), 7.30–7.14 (m, 8H; PC_6H_4), 7.06 (d, J = 7.7 Hz, 2H; OC_6H_3), 6.86–6.78 (m, 2H; OC_6H_3), 6.46 (d, J = 9.2 Hz, 2H; OC_6H_3), 3.52 (s, 8H; CH_2N), 2.48 (q, J = 7.4 Hz, 16H; CH_2CH_3), 2.00 (s, 6H; CH_3), 1.00 ppm (t, J = 7.0 Hz, 24H; CH_2CH_3); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 293 K): δ = 19.2 ppm (s); HRMS (FAB+): m/z calcd for $[C_{58}H_{76}Cl_2N_4OP_2Pd-Cl]^+$: 1047.4235; found: 1047.4235.

*cis-[PdCl$_2$(**A-HOTs**)] (**1(A-HOTs)**)*

p-Toluenesulfonic acid monohydrate (29.6 mg, 155.4 μmol) was added to a solution of **1a** (35.6 mg, 38.9 μmol) in methanol (3 mL). The reaction mixture was stirred for 1 h at room temperature. Next, the solvent was evaporated, and pentane was added to the solid precipitate. After evaporation of the solvent in vacuo, the product **1(A-HOTs)** was obtained as a yellow powder in quantitative yield. ^{1}H NMR (300 MHz, CD_3OD, 293 K): δ = 8.06–7.93 (m, 8H; PC_6H_4), 7.69 (d, J = 6.8 Hz, 8H; PC_6H_4), 7.64 (d, J = 7.9 Hz, 8H; OTs^-), 7.21 (d, J = 7.9 Hz, 8H; OTs^-), 4.38 (s, 8H; CH_2N), 3.29–3.05 (m, 16H; CH_2CH_3), 2.89–2.72 (m, 4H; CH_2CH_2), 2.32 (s, 12H; CH_3, OTs^-), 1.29 ppm (t, J = 6.9 Hz, 24H; CH_2CH_3); ^{13}C{^{1}H} NMR (75 MHz, CD_3OD, 293 K): δ = 142.2 (s; OTs^-), 140.6 (s; OTs^-), 134.4 (brs), 131.6 (brs), 129.8 (s), 129.1 (s), 128.7 (s; OTs^-), 125.6 (s; OTs^-), 55.1 (s; CH_2N), 46.9 (s; CH_2CH_3), 28.0 (brs; CH_2CH_2), 20.1 (s; CH_3, OTs^-), 7.7 ppm (s; CH_2CH_3); ^{31}P{^{1}H} NMR (121.5 MHz, CD_3OD, 293 K): δ = 68.3 ppm (s); HRMS (FAB+): m/z calcd for $[C_{74}H_{100}Cl_2N_4O_{12}P_2PdS_4-C_{28}H_{32}S_4O_{12}Cl]^+$: 879.3656; found: 879.3665; ESI-MS: (m/z, CH_3OH) calcd for $[C_{74}H_{100}Cl_2N_4O_{12}P_2PdS_4-C_{14}H_{14}S_2O_6]^{2+}$: 630.20; found: 630.21.

*cis-[PdCl$_2$(**B-HOTs**)] (**1(B-HOTs)**)*

p-Toluenesulfonic acid monohydrate (18.0 mg, 94.4 μmol) was added to a solution of **1b** (25.6 mg, 23.6 μmol) in dichloromethane (3 mL). The reaction mixture was stirred for 2 h at room temperature. Next, the solvent was evaporated, and pentane was added to the solid precipitate. After evaporation of the solvent in vacuo, the product **1(B-HOTs)** was obtained as an orange powder in quantitative yield. ^{1}H NMR (300 MHz, CD_3OD, 293 K): δ = 7.66 (d, J = 8.3 Hz, 8H; OTs^-), 7.60 (m, 16H; PC_6H_4), 7.30 (d, J = 8.3 Hz, 2H; OC_6H_3), 7.20 (d, J = 7.9 Hz, 8H; OTs^-), 6.95 (m, 2H; OC_6H_3), 6.50 (d, J = 10.0 Hz, 2H; OC_6H_3), 4.36 (dd, J = 13.3 Hz and 18.8 Hz, 8H; CH_2N), 3.31–3.03 (m, 16H; CH_2CH_3), 2.32 (s, 12H; CH_3, OTs^-), 2.05 (s, 6H; CH_3), 1.28 ppm (t, J = 7.3 Hz, 24H; CH_2CH_3); ^{31}P{^{1}H} NMR (121.5 MHz, CD_3OD, 293 K): δ = 20.3 ppm (s); HRMS (FAB+): m/z calcd for $[C_{86}H_{108}Cl_2N_4O_{13}P_2PdS_4-C_{28}H_{32}S_4O_{12}Cl]^+$: 1047.4235; found: 1047.4226; ESI-MS: (m/z, CH_3OH) calcd for $[C_{86}H_{108}Cl_2N_4O_{13}P_2PdS_4-C_{14}H_{14}S_2O_6Cl]^{3+}$: 464.49; found: 464.48.

*cis-[PdCl$_2$(**A-MeOTf**)] (**1(A-MeOTf)**)*

Methyl trifluoromethanesulfonate (0.34 mL, 3.00 mmol) was added dropwise to a solution of **1a** (0.46 g, 0.50 mmol) in dichloromethane (20 mL), which resulted in some orange precipitation. The reaction mixture was stirred for 2 h at room temperature. Next, the solution was concentrated to 2 mL, and diethyl ether (10 mL) was added, which resulted in more precipitation. The supernatant was removed, and the crude product was washed twice with diethyl ether and dried in vacuo. The product **1(A-MeOTf)** was obtained as an off-white fine powder (0.75 g, 0.48 mmol, 96 %). ^{1}H NMR (300 MHz, CD_3OD, 293 K): δ = 8.10–7.97 (m, 8H; PC_6H_4), 7.75 (d, J = 7.0 Hz, 8H; PC_6H_4), 4.56 (s, 8H; CH_2N), 3.39 (m, 16H; CH_2CH_3), 2.95 (s, 12H; NCH_3), 2.96–2.78 (m, 4H; CH_2CH_2), 1.41 ppm (t, J = 7.2 Hz, 24H; CH_2CH_3); ^{13}C{^{1}H} NMR (75 MHz, CD_3OD, 293 K): δ = 133.9 (brs), 132.1 (s), 130.3 (s), 129.6 (s), 120.5 (q, J = 319 Hz; CF_3), 63.6 (s; NCH_3), 55.9 (s; CH_2N), 46.0 (s; CH_2CH_3), 27.8 (brs; CH_2CH_2), 6.9 ppm (s; CH_2CH_3); ^{31}P{^{1}H} NMR (121.5 MHz, CD_3OD, 293 K): δ = 69.3 ppm (s); ^{19}F NMR (282 MHz, CD_3OD, 293 K): δ = −77.8 ppm (s); HRMS (FAB+): m/z calcd for $[C_{54}H_{80}Cl_2F_{12}N_4O_{12}P_2PdS_4-CF_3SO_3]^+$: 1423.2832; found: 1423.2822.

*cis-[PdCl$_2$(**B-MeOTf**)] (**1(B-MeOTf)**)*

This compound was prepared similarly to **1(A-MeOTf)**. The product was obtained as an ochre fine powder (92 %). ^{1}H NMR (300 MHz, CD_3OD, 293 K): δ = 7.74–7.61 (m, 16H; PC_6H_4), 7.33 (d, J = 8.3 Hz, 2H; OC_6H_3), 7.03–6.95 (m, 2H; OC_6H_3), 6.58 (d, J = 10.5 Hz, 2H; OC_6H_3), 4.53 (dd, J = 12.9 Hz and 24.2 Hz, 8H; CH_2N), 3.75–3.50 (m, 16H; CH_2CH_3), 2.93 (s, 12H; NCH_3), 2.07 (s, 12H; CH_3), 1.40 ppm (t, J = 6.7 Hz, 24H; CH_2CH_3); ^{31}P{^{1}H} NMR (121.5 MHz, CD_3OD, 293 K): δ = 21.2 ppm (s); ^{19}F NMR (282 MHz, CD_3OD, 293 K): δ = −80.4 ppm (s); HRMS (FAB+): m/z calcd for $[C_{66}H_{88}Cl_2F_{12}N_4O_{13}P_2PdS_4-CF_3SO_3]^+$: 1591.3411; found: 1591.3403.

*5,11,17,23-Tetrakis(sulfonic acid)-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene (**2-SO$_3$H**)*

The strongly acidic Amberlyst 15 ion-exchange resin (3.6 g; macroreticular resin with sulfonic acid functionality) was added to a white suspension of tetrasulfonatocalix[4]arene tetrasodium salt **2-SO$_3$Na** (2.02 g, 1.80 mmol) in methanol (35 mL). The reaction mixture was stirred for 1 h at room temperature. Subsequently, the clear pale yellow solution was filtered, and upon evaporation of the solvent in vacuo, the product **2-SO$_3$H** was obtained as a brown sticky solid in quantitative yield. ^{1}H NMR (300 MHz, CD_3OD, 293 K): $\delta = 7.38$ (s, 8H; H_{Ar}), 4.74 (d, $J = 12.8$ Hz, 4H; C*H*H′), 4.31 (t, $J = 5.0$ Hz, 8H; OCH_2CH_2), 3.91 (t, $J = 5.0$ Hz, 8H; OCH_2CH_2), 3.56 (q, $J = 7.0$ Hz, 8H; OCH_2CH_3), 3.39 (d, $J = 12.9$ Hz, 4H; CH*H*′), 1.22 ppm (t, $J = 7.0$ Hz, 12H; OCH_2CH_3); ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): $\delta = 11.0$ ppm (br s, SO_3H); $^{13}C\{^1H\}$ NMR (75 MHz, CD_3OD, 293 K): $\delta = 158.8$ (s; Cq, C_{Ar}), 136.7 (s; Cq, C_{Ar}), 135.0 (s; Cq, C_{Ar}), 126.4 (s; CH, C_{Ar}), 73.8 (s; CH_2), 69.6 (s; CH_2), 66.3 (s; CH_2), 30.8 (s; ArCH_2Ar), 14.8 ppm (s; CH_3).

General Procedure for the Self-Assembly of the Diphosphine Capsules by the Using Precharged Building Blocks

Capsule self-assembly was done in situ. Equimolar methanol solutions of the tetracationic diphosphine (**A-HCl** or **B-HCl** or **C-HCl**) and the tetraanionic calix[4]arene **2-SO$_3$Na** were mixed at room temperature, thereby resulting in the immediate formation of the corresponding capsule (**(A-HCl)·2**, **(B-HCl)·2**, and **(C-HCl)·2** respectively). Self-assembly of capsules **(D-HCl)·2** and **(E-HCl)·2** was done in a similar way.

General Procedure for the Self-Assembly of the Diphosphine Capsules by the Use of Neutral Building Blocks

A methanol solution of the tetraacidic calix[4]arene **2-SO$_3$H** (1 equiv) was slowly added to a methanol solution of the tetraamine diphosphine (**a** or **b** or **c**; 1 equiv). The solution was stirred for 30 min at room temperature, and subsequently the solvent was evaporated, thereby resulting in the corresponding capsule (**(A)·2**, **(B)·2**, and **(C)·2** respectively).

General Procedure for the Self-Assembly of Pd Capsules by Using Precharged Building Blocks

Capsule self-assembly was done in situ. Equimolar methanol solutions of the palladium tetracationic-diphosphine complex (**1(A-MeOTf)** or **1(B-MeOTf)**) and the tetraanionic calix[4]arene **2-SO$_3$Na** were mixed at room temperature, thereby resulting in the immediate formation of the corresponding capsule (**1(A-MeOTf)·2** and **1(B-MeOTf)·2**, respectively).

*Self-Assembly of Pd Capsules by Using Neutral Building Blocks (Capsule **1(A)·2**)*

An equimolar solution of tetraacidic calix[4]arene **2-SO$_3$H** (1 equiv) in methanol was slowly added to a methanol solution of **1a** (1 equiv), upon which some precipitation appeared. The reaction mixture was stirred for 30 min at room temperature, and subsequently the solvent was evaporated, thereby resulting in capsule **1(A)·2**.

*Self-Assembly of Pd Capsules by the Use of Neutral Building Blocks (Capsule **1(B)·2**)*

An equimolar solution of tetraacidic calix[4]arene **2-SO$_3$H** (1 equiv) in dichloromethane was slowly added to a solution of **1b** (1 equiv) in dichloromethane, upon which precipitation appeared. The reaction mixture was stirred for 30 min at room temperature, and subsequently the solvent was evaporated, thereby resulting in capsule **1(B)·2**. Note: self-assembly of capsule **1(B)·2** was done in dichloromethane because of the instability of **1b** in methanol. After the capsule was formed, the capsule was stable and soluble in MeOH/CH_2Cl_2 or MeOH/H_2O mixtures.

NMR Spectroscopic Characterization of the Capsules

Upfield shifts ($\Delta\delta_H$) of the $CH_2N(H^+/CH_3^+)(CH_2CH_3)_2$ protons of the bound PP or Pd(PP) building blocks upon capsule formation are given, with respect to those of the corresponding free building blocks (for capsules assembled from neutral building blocks, $\Delta\delta_H$ is calculated with respect to the corresponding protonated building blocks; Table 3). Some of the proton resonances were not visible because they overlap with other signals or are very broad, or because of H–D exchange with CD_3OD. Capsule **(D-HCl)·2** did not show significant upfield shifts upon capsule formation ($\Delta\delta_H \leq 0.07$ ppm). Capsule **(E-HCl)·2**: $\Delta\delta(N(CH_3)_2) = 0.51$ ppm in CD_3OD and $\Delta\delta(NH) = 0.55$ ppm in [D_6]DMSO. The phosphorus chemical shifts of the diphosphines **A**–**E** and the Pd–diphosphines **1A** and **1B** in their capsular form did not exhibit a noteworthy shift compared to the monomeric form ($\Delta\delta \leq 0.8$ ppm).

Table 3. Observed upfield shifts ($\Delta\delta$H) of the $CH_2N(H^+/CH_3^+)(CH_2CH_3)_2$ protons upon capsule formation.[a]

Capsule	PP/**2**	$\Delta\delta(CH_2CH_3)$ [ppm]	$\Delta\delta(CH_2CH_3)$ [ppm]	$\Delta\delta(CH_2N)$ [ppm]	$\Delta\delta(NCH_3)$ [ppm]
(A-HCl)·2[b]	1:3	0.46	0.31	0.15	–
(B-HCl)·2[b]	1:3	0.42	0.32	0.20	–
(C-HCl)·2[b]	1:3	0.43	0.33	0.25	–
(A)·2[b]	1:1	0.43	0.33	0.18	–
(B)·2[b]	1:1	0.39	0.32	0.22	–
(C)·2[b]	1:1	0.40	0.35	0.27	–
1(A-MeOTf)·2[c]	1:2	0.35	0.16	0.06	0.13
1(B-MeOTf)·2[c]	1:2	0.35	n.o.	n.o.	0.10
1(A)·2[d]	1:1	0.33	0.22	0.11	–
1(B)·2[d]	1:1	0.37	0.23	0.12	–

[a] [PP] or [Pd(PP)] = 2 mM; n.o. = not observed. [b] In CD_3OD, at 20 °C. [c] In CD_3OD at 60 °C. [d] In CD_3OD/D_2O (8:2 mol %) at 40 °C.

Job Plot

Equimolar solutions (2 mM) of **1(PP)** and **2-SO$_3$Na** in CD_3OD were prepared and mixed in various ratios. In this way the total concentration of **1(PP)** and **2** was kept constant at 2 mM and only the **1(PP)/2** ratio was varied. ^{1}H NMR spectra of the mixtures were recorded at 60 °C, and the chemical shifts of **1(PP)** were analyzed by Job's method of continuous variation, that is, a plot of the capsule concentration as a function of the mole fraction of **2**,[27] **1(PP)** = **1(A-MeOTf)**, or **1(B-MeOTf)**.

^{1}H NMR Spectroscopic Titrations

The ^{1}H NMR spectroscopic titrations of **2-SO$_3$Na** with **A-HCl** and of **2-SO$_3$Na** with **B-HCl** were measured in CD_3OD at 298 K under inert conditions. Because of solubility reasons the concentration of **2** was kept constant and low in all the samples (1 mM), whereas the concentrations of **A-HCl** and **B-HCl** were varied from 0 to 3 mM. The chemical shifts of the diphosphine protons $CH_2NH^+(CH_2CH_3)_2$ of **(A-HCl)·2** and **(B-HCl)·2**, relative to the chemical shifts of **A-HCl** and **B-HCl**, respectively, were followed and fitted to a 1:1 binding model by using a least-squares fitting procedure.[21b] The association constants K for a single run were calculated as the mean of the values obtained for each of the followed diphosphine signals, weighted by the observed changes in chemicals shift.[28] The association constants from different runs were then averaged. The association constant found for capsule **(A-HCl)·2** is $K_{A\text{-}2} = 3 \times 10^4\ M^{-1}$ and for capsule **(B-HCl)·2** is $K_{B\text{-}2} = 8 \times 10^4\ M^{-1}$. Lines in the titration curves are best-fit curves calculated by nonlinear regression.

ESI-MS Measurements

Samples of the capsules (PP/calix = 1:1–1:3) with initial concentrations of 100–250 μM were diluted in MeOH to a final concentration of 1%. Comparison of the measured isotope patterns of the capsules with the calculated ones confirm their elemental composition and charge state. The ion

peaks of the capsules correspond to 1:1 complexes, and no ion peaks for higher aggregates were detected. From the survey MS spectra, individual candidate ions were selected for collision-induced dissociation (CID) MS/MS with Argon as collision gas. The assignment of the ion peaks of the capsule is confirmed by CID experiments: upon collision-induced dissociation of the ion peaks of the capsule, product peaks appeared that correspond to the building blocks of the capsule. The reported *m*/*z* values correspond to the 100% ion peak (isotope with the highest intensity). Capsule **(A-HCl)·2** ($C_{90}H_{124}N_4O_{20}P_2S_4$): ESI-MS ($CH_3OH$): *m*/*z*: calcd for $[\mathbf{A{\cdot}2}+2Na]^{2+}$: 908.85; found: 908.95; calcd for $[\mathbf{A{\cdot}2}+Na+H]^{2+}$: 897.86; found: 897.93; calcd for $[\mathbf{A{\cdot}2}+2H]^{2+}$: 886.37; found: 886.42. Capsule **(B-HCl)·2** ($C_{102}H_{132}N_4O_{21}P_2S_4$): ESI-MS ($CH_3OH$): *m*/*z*: calcd for $[\mathbf{B{\cdot}2}+H+Na]^{2+}$: 981.89; found: 981.99; calcd for $[\mathbf{B{\cdot}2}+2H]^{2+}$: 970.90; found: 970.97; calcd for $[\mathbf{B{\cdot}2}+2H+Na]^{3+}$: 654.93; found: 654.99; calcd for $[\mathbf{B{\cdot}2}+3H]^{3+}$: 647.60; found: 647.66. Capsule **(C-HCl)·2** ($C_{103}H_{132}N_4O_{21}P_2S_4$): ESI-MS ($CH_3OH$): *m*/*z*: calcd for $[\mathbf{C{\cdot}2}+3H]^{3+}$: 651.265; found: 651.263; calcd for $[\mathbf{C{\cdot}2}+2H+1Na]^{3+}$: 658.593; found: 658.602; calcd for $[\mathbf{C{\cdot}2}+1H+2Na]^{3+}$: 665.920; found: 665.921; calcd for $[\mathbf{C{\cdot}2}+3Na]^{3+}$: 673.247; found: 673.251; calcd for $[\mathbf{C{\cdot}2}+2H]^{2+}$: 976.394; found: 976.354; calcd for $[\mathbf{C{\cdot}2}+1H+1Na]^{2+}$: 987.385; found: 987.327; calcd for $[\mathbf{C{\cdot}2}+2Na]^{2+}$: 998.375; found: 998.325. Capsule **(D-HCl)·2** ($C_{91}H_{108}N_4O_{21}P_2S_4$): ESI-MS ($CH_3OH$): *m*/*z*: calcd for $[\mathbf{D{\cdot}2}+2Na]^{2+}$: 914.78; found: 914.98; calcd for $[\mathbf{D{\cdot}2}+Na+H]^{2+}$: 903.79; found: 903.99; calcd for $[\mathbf{D{\cdot}2}+2H]^{2+}$: 892.80; found: 893.00. Capsule **(E-HCl)·2** ($C_{103}H_{132}N_{12}O_{21}P_2S_4$): ESI-MS ($CH_3OH$): *m*/*z*: calcd for $[\mathbf{E{\cdot}2}+2Na]^{2+}$: 1054.89; found: 1055.13; calcd for $[\mathbf{E{\cdot}2}+Na+H]^{2+}$: 1043.90; found: 1044.11; calcd for $[\mathbf{E{\cdot}2}+2H]^{2+}$: 1032.91; found: 1033.16; calcd for $[\mathbf{E{\cdot}2}+3Na]^{3+}$: 710.92; found: 711.07; calcd for $[\mathbf{E{\cdot}2}+2Na+H]^{3+}$: 703.60; found: 703.77; calcd for $[\mathbf{E{\cdot}2}+Na+2H]^{3+}$: 696.27; found: 696.44. Capsule **1(A-MeOTf)·2** ($C_{94}H_{132}N_4O_{20}P_2PdS_4Cl_2$): ESI-MS ($CH_3OH$): *m*/*z*: calcd for $[\mathbf{1(A\text{-}MeOTf){\cdot}2}-2Cl]^{2+}$: 967.34; found: 967.38; calcd for $[\mathbf{1(A\text{-}MeOTf){\cdot}2}-2Cl+Na]^{3+}$: 652.56; found: 652.60; calcd for $[\mathbf{1(A\text{-}MeOTf){\cdot}2}-2Cl+H]^{3+}$: 645.23; found: 645.24. Capsule **1(A)·2** ($C_{90}H_{124}Cl_2N_4O_{20}P_2PdS_4$): ESI-MS ($CH_3OH$): *m*/*z*: calcd for $[\mathbf{1(A){\cdot}2}-Cl+H]^{2+}$: 957.30; found: 957.30; calcd for $[\mathbf{1(A){\cdot}2}-2Cl]^{2+}$: 938.31; found: 938.31; calcd for $[\mathbf{1(A){\cdot}2}-2Cl+H]^{3+}$: 625.88; found: 625.88. Capsule **1(B-MeOTf)·2** ($C_{106}H_{140}Cl_2N_4O_{21}P_2PdS_4$): ESI-MS ($CH_3OH$): *m*/*z*: calcd for $[\mathbf{1(B\text{-}MeOTf){\cdot}2}-Cl+2H]^{3+}$: 713.24; found: 713.26; calcd for $[\mathbf{1(B\text{-}MeOTf){\cdot}2}-2Cl+H]^{3+}$: 701.25; found: 701.28. Capsule **1(B)·2** ($C_{102}H_{132}N_4O_{21}P_2PdS_4Cl_2$): ESI-MS ($CH_3OH$): *m*/*z*: calcd for $[\mathbf{1(B){\cdot}2}-Cl+H]^{2+}$: 1041.33; found: 1041.36; calcd for $[\mathbf{1(B){\cdot}2}-2Cl]^{2+}$: 1023.34; found: 1023.37; calcd for $[\mathbf{1(B){\cdot}2}-Cl+2H]^{3+}$: 694.55; found: 694.58; calcd for $[\mathbf{1(B){\cdot}2}-2Cl+H]^{3+}$: 682.56; found: 682.58.

[1] a) T. S. Koblenz, J. Wassenaar, J. N. H. Reek, *Chem. Soc. Rev.* **2008**, *37*, 247–262; b) "Chemistry in Self-Assembled Nanoreactors": J. I. Van Der Vlugt, T. S. Koblenz, J. Wassenaar, J. N. H. Reek in *Molecular Encapsulation: Organic Reactions in Constrained Systems* (Eds.: U. H. Brinker, J.-L. Mieusset), Wiley, Chichester, UK, **2010**, p. 145–174; c) F. Hof, S. L. Craig, C. Nuckolls, J. Rebek, Jr., *Angew. Chem.* **2002**, *114*, 1556–1578; *Angew. Chem. Int. Ed.* **2002**, *41*, 1488–1508; d) M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa, K. Biradha, *Chem. Commun.* **2001**, 509–518; e) J. Rebek, Jr., *Angew. Chem.* **2005**, *117*, 2104–2115; *Angew. Chem. Int. Ed.* **2005**, *44*, 2068–2078; f) M. M. Conn, J. Rebek, Jr., *Chem. Rev.* **1997**, *97*, 1647–1668; g) A. Lützen, *Angew. Chem.* **2005**, *117*, 1022–1025; *Angew. Chem. Int. Ed.* **2005**, *44*, 1000–1002; h) J. Chen, J. Rebek, Jr., *Org. Lett.* **2002**, *4*, 327–329; i) M. Yoshizawa, Y. Takeyama, T. Okano, M. Fujita, *J. Am. Chem. Soc.* **2003**, *125*, 3243–3247; j) D. M. Vriezema, M. C. Aragones, J. A. A. W. Elemans, J. J. L. M. Cornelissen, A. E. Rowan, R. J. M. Nolte, *Chem. Rev.* **2005**, *105*, 1445–1489; k) J.-L. Hou, D. Ajami, J. Rebek, Jr., *J. Am. Chem. Soc.* **2008**, *130*, 7810–7811; l) A. Natarajan, L. S. Kaanumalle, S. Jockusch, C. L. D. Gibb, B. C. Gibb, N. J. Turro, V. Ramamurthy, *J. Am. Chem. Soc.* **2007**, *129*, 4132–4133; m) M. D. Pluth, R. G. Bergman, K. N. Raymond, *J. Am. Chem. Soc.* **2008**, *130*, 11423–11429; n) C. J. Hastings, D. Fiedler, R. G. Bergman, K. N. Raymond, *J. Am. Chem. Soc.* **2008**, *130*, 10977–10983; o) M. Yoshizawa, M. Tamura, M. Fujita, *Science* **2006**, *312*, 251–254; p) H. Ito, T. Kusukawa, M. Fujita, *Chem. Lett.* **2000**, *29*, 598–599; q) M. Yoshizawa, T. Kusukawa, M. Fujita, S. Sakamoto, K. Yamaguchi, *J. Am. Chem. Soc.* **2001**, *123*, 10454–10459; r) Y. Nishioka, T. Yamaguchi, M. Kawano, M. Fujita, *J. Am. Chem. Soc.* **2008**, *130*, 8160–8161.

[2] Capsules based on hydrogen bonds: a) S. K. Körner, F. C. Tucci, D. M. Rudkevich, T. Heinz, J. Rebek, Jr., *Chem. Eur. J.* **2000**, *6*, 187–195; b) D. Ajami, J. Rebek, Jr., *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 16000–16003; c) R. K. Castellano, B. H. Kim, J. Rebek, Jr., *J. Am. Chem. Soc.* **1997**, *119*, 12671–12672; d) M. Bolte, I. Thondorf, V. Boehmer, V. Rudzevich, Y. Rudzevich, *CrystEngComm* **2008**, *10*, 270–272; e) D. Ajami, M. P. Schramm, A. Volonterio, J. Rebek, Jr., *Angew. Chem.* **2007**, *119*, 246–248; *Angew. Chem. Int. Ed.* **2007**, *46*, 242–244; f) S. Ma, D. M. Rudkevich, J. Rebek, Jr., *J. Am. Chem. Soc.* **1998**, *120*, 4977–4981; g) A. Shivanyuk, J. Rebek, Jr., *Chem. Commun.* **2001**, 2424–2425; h) J. Kang, J. Santamaria, G. Hilmersson, J. Rebek, Jr., *J. Am. Chem. Soc.* **1998**, *120*, 7389–7390; i) J. L. Atwood, L. J. Barbour, A. Jerga, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4837–4841.

[3] Capsules based on metal–ligand bonds: a) F. Fochi, P. Jacopozzi, E. Wegelius, K. Rissanen, P. Cozzini, E. Marastoni, E. Fisicaro, P. Manini, R. Fokkens, E. Dalcanale, *J. Am. Chem. Soc.* **2001**, *123*, 7539–7552; b) M. Fujita, M. Tominaga, A. Hori, B. Therrien, *Acc. Chem. Res.* **2005**, *38*, 369–378; c) K. Suzuki, J. Iida, S. Sato, M. Kawano, M. Fujita, *Angew. Chem.* **2008**, *120*, 5864–5866; *Angew. Chem. Int. Ed.* **2008**, *47*, 5780–5782; d) L. Pirondini, D. Bonifazi, B. Cantadori, P. Braiuca, M. Campagnolo, R. De Zorzi, S, Geremia, F. Diederich, E. Dalcanale, *Tetrahedron* **2006**, *62*, 2008–2015; e) S. J. Park, O. H. Kwon, K. S Lee, K. Yamaguchi, D. J. Jang, J. I. Hong, *Chem. Eur. J.* **2008**, *14*, 5353–5359; f) T. Haino, M. Kobayashi, Y. Fukazawa, *Chem. Eur. J.* **2006**, *12*, 3310–3319; g) Z. Zhong, A. Ikeda, M. Ayabe, S. Shinkai, S. Sakamoto, K. Yamaguchi, *J. Org. Chem.* **2001**, *66*, 1002–1008; h) M. L. Merlau, M. Del Pilar Mejia, S. T. Nguyen, J. T. Hupp, *Angew. Chem.* **2001**, *113*, 4369–4372; *Angew. Chem. Int. Ed.* **2001**, *40*, 4239–4242; i) S. J. Lee, K. L. Mulfort, X. Zuo, A. J. Goshe, P. J. Wesson, S. T. Nguyen, J. T. Hupp, D. M. Tiede, *J. Am. Chem. Soc.* **2008**, *130*, 836–838; j) D. Fiedler, D. H. Leung, R. G. Bergman, K. N. Raymond, *Acc. Chem. Res.* **2005**, *38*, 349–358; k) R. M. McKinlay, P. K. Thallapally, G. W. V. Cave, J. L. Atwood, *Angew. Chem.* **2005**, *117*, 5879–5882; *Angew. Chem. Int. Ed.* **2005**, *44*, 5733–5736; l) S. J. Dalgarno, N. P. Power, J. L. Atwood, *Coord. Chem. Rev.* **2008**, *252*, 825–841.

[4] Capsules based on ionic interactions: a) R. Zadmard, M. Junkers, T. Schrader, T. Grawe, A. Kraft, *J. Org. Chem.* **2003**, *68*, 6511–6521; b) R. Fiammengo, P. Timmerman, J. Huskens, K. Versluis, A. J. R. Heck, D. N. Reinhoudt, *Tetrahedron* **2002**, *58*, 757–764; c) F. Corbellini, R. Fiammengo, P. Timmerman, M. Crego-Calama, K. Versluis, A. J. R. Heck, I. Luyten, D. N. Reinhoudt, *J. Am. Chem. Soc.* **2002**, *124*, 6569–6575; d) F. Corbellini, R. M. A. Knegtel, P. D. J. Grootenhuis, M. Crego-Calama, D. N. Reinhoudt, *Chem. Eur. J.* **2005**, *11*, 298–307; e) G. V. Oshovsky, D. N. Reinhoudt, W. Verboom, *J. Am. Chem. Soc.* **2006**, *128*, 5270–5278; f) B. Kuberski, A. Szumna, *Chem. Commun.* **2009**, 1959–1961; g) R. Fiammengo, K. Wojciechowski, M. Crego-Calama, P. Timmerman, A. Figoli, M. Wessling, D. N. Reinhoudt, *Org. Lett.* **2003**, *5*, 3367–3370; h) R. Zadmard, T. Schrader, T. Grawe, A. Kraft, *Org. Lett.* **2002**, *4*, 1687–1690.

[5] a) T. S. Koblenz, H. L. Dekker, C. G. De Koster, P. W. N. M. Van Leeuwen, J. N. H. Reek, *Chem. Commun.* **2006**, 1700–1702; b) T. S. Koblenz, PhD thesis, University of Amsterdam, The Netherlands, **2010**.

[6] a) D. H. Leung, R. G. Bergman, K. N. Raymond, *J. Am. Chem. Soc.* **2006**, *128*, 9781–9797; b) D. H. Leung, R. G. Bergman, K. N. Raymond, *J. Am. Chem. Soc.* **2007**, *129*, 2746–2747; c) V. F. Slagt, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. Van Leeuwen, *Angew. Chem.* **2001**, *113*, 4401–4404; *Angew. Chem. Int. Ed.* **2001**, *40*, 4271–4274; d) V. F. Slagt, P. W. N. M. van Leeuwen, J. N. H. Reek, *Angew. Chem.* **2003**, *115*, 5777–5781; *Angew. Chem. Int. Ed.* **2003**, *42*, 5619–5623; e) V. F. Slagt, P. C. J. Kamer, P. W. N. M. Van Leeuwen, J. N. H. Reek, *J. Am. Chem. Soc.* **2004**, *126*, 1526–1536; f) A. W.

Kleij, M. Lutz, A. L. Spek, P. W. N. M. van Leeuwen, J. N. H. Reek, *Chem. Commun.* **2005**, 3661–3663; g) A. W. Kleij, J. N. H. Reek, *Chem. Eur. J.* **2006**, *12*, 4218–4227; h) A. W. Kleij, M. Kuil, D. M. Tooke, A. L. Spek, J. N. H. Reek, *Inorg. Chem.* **2005**, *44*, 7696–7698; i) M. Kuil, T. Soltner, P. W. N. M. Van Leeuwen, J. N. H. Reek, *J. Am. Chem. Soc.* **2006**, *128*, 11344–11345; j) J. Flapper, J. N. H. Reek, *Angew. Chem.* **2007**, *119*, 8744–8746; *Angew. Chem. Int. Ed.* **2007**, *46*, 8590–8592; k) L. R. MacGillivray, H. A. Spinney, J. L. Reid, J. A. Ripmeester, *Chem. Commun.* **2000**, 517–518.

[7] P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *Acc. Chem. Res.* **2001**, *34*, 895–904.

[8] a) A. Buhling, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. W. Elgersma, K. Goubitz, J. Fraanje, *Organometallics* **1997**, *16*, 3027–3037; b) P. Dierkes, S. Ramdeehul, L. Barloy, A. De Cian, J. Fischer, P. C. J. Kamer, P. W. N. M. Van Leeuwen, J. A. Osborn, *Angew. Chem.* **1998**, *110*, 3299–3301; *Angew. Chem. Int. Ed.* **1998**, *37*, 3116–3118; c) H. Ito, A. Watanabe, M. Sawamura, *Org. Lett.* **2005**, *7*, 1869–1871; d) M. S. Goedheijt, B. E. Hanson, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. Van Leeuwen, *J. Am. Chem. Soc.* **2000**, *122*, 1650–1657.

[9] a) A. M. Kluwer, I. Ahmad, J. N. H. Reek, *Tetrahedron Lett.* **2007**, *48*, 2999–3001; b) J. Chatt, W. Hussain, G. J. Leigh, H. M. Ali, C. J. Pickett, D. A. Rankin, *J. Chem. Soc. Dalton Trans.* **1985**, 1131–1136.

[10] a) M. Caporali, C. Müller, B. B. P. Staal, D. M. Tooke, A. L. Spek, P. W. N. M. van Leeuwen, *Chem. Commun.* **2005**, 3478–3480; b) E. Guiu, M. Caporali, B. Munoz, C. Müller, M. Lutz, A. L. Spek, C. Claver, P. W. N. M. Van Leeuwen, *Organometallics* **2006**, *25*, 3102–3104.

[11] A. Buhling, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Mol. Catal. A* **1995**, *98*, 69–80.

[12] a) R. Dorta, L. Shimon, D. Milstein, *J. Organomet. Chem.* **2004**, *689*, 751–758; b) G. Arena, A. Casnati, A. Contino, A. Magri, F. Sansone, D. Sciotto, R. Ungaro, *Org. Biomol. Chem.* **2006**, *4*, 243–249.

[13] a) F. Corbellini, F. W. B. van Leeuwen, H. Beijleveld, H. Kooijman, A. L. Spek, W. Verboom, M. Crego-Calama, D. N. Reinhoudt, *New J. Chem.* **2005**, *29*, 243–248; b) G. V. Oshovsky, D. N. Reinhoudt, W. Verboom, *Eur. J. Org. Chem.* **2006**, *12*, 2810–2816.

[14] a) *High-Resolution NMR Techniques in Organic Chemistry* (Ed.: T. Claridge), Elsevier, Amsterdam, **2000**; b) D. Neuhaus, M. P. Williamson, *The Nuclear Overhauser Effect in Structural and Conformational Analysis*, 2nd ed., Wiley-VCH, New York, **2000**; c) A. Shivanyuk, J. Rebek, Jr., *J. Am. Chem. Soc.* **2003**, *125*, 3432–3433; d) A. Shivanyuk, M. Saadioui, F. Broda, I. Thondorf, M. O. Vysotsky, K. Rissanen, E. Kolehmainen, V. Boehmer, *Chem. Eur. J.* **2004**, *10*, 2138–2148.

[15] a) C. A. Schalley, R. K. Castellano, M. S. Brody, D. M. Rudkevich, G. Siuzdak, J. Rebek, Jr., *J. Am. Chem. Soc.* **1999**, *121*, 4568–4579; b) R. Zadmard, A. Kraft, T. Schrader, U. Linne, *Chem. Eur. J.* **2004**, *10*, 4233–4239; c) D. P. Weimann, C. A. Schalley, *Supramol. Chem.* **2008**, *20*, 117–128.

[16] a) T. Grawe, T. Schrader, M. Gurrath, A. Kraft, F. Osterod, *Org. Lett.* **2000**, *2*, 29–32; b) T. Grawe, T. Schrader, R. Zadmard, A. Kraft, *J. Org. Chem.* **2002**, *67*, 3755–3763; c) B. M. O'Leary, T. Szabo, N. Svenstrup, C. A. Schalley, A. Lutzen, M. Schäfer, J. Rebek, Jr., *J. Am. Chem. Soc.* **2001**, *123*, 11519–11533.

[17] a) A. Hessler, O. Stelzer, H. Dibowski, K. Worm, F. P. Schmidtchen, *J. Org. Chem.* **1997**, *62*, 2362–2369; b) M. A. Zuideveld, B. H. G. Swennenhuis, M. D. K. Boele, Y. Guari, G. P. F. van Strijdonck, J. N. H. Reek, P. C. J. Kamer, K. Goubitz, J. Fraanje, M. Lutz, A. L. Spek, P. W. N. M. van Leeuwen, *J. Chem. Soc. Dalton Trans.* **2002**, 2308–2317.

[18] a) P. Wasserscheid, H. Waffenschmidt, P. Machnitzki, K. W. Kottsieper, O. Stelzer, *Chem. Commun.* **2001**, 451–452; b) P. Machnitzki, M. Tepper, K. Wenz, O. Stelzer, E. Herdtweck, *J. Organomet. Chem.* **2000**, *602*, 158–169; c) T. Suhs, B. Koenig, *Mini-Rev. Org. Chem.* **2006**, *3*, 315–331.

[19] D. Cuc, S. Bouguet-Bonnet, N. Morel-Desrosiers, J.-P. Morel, P. Mutzenhardt, D. Canet, *J. Phys. Chem. B* **2009**, *113*, 10800–10807.

[20] H. Gulyás, J. Benet-Buchholz, E. C. Escudero-Adan, Z. Freixa, P. W. N. M. van Leeuwen, *Chem. Eur. J.* **2007**, *13*, 3424–3430.

[21] a) P. Blondeau, M. Segura, R. Perez-Fernandez, J. De Mendoza, *Chem. Soc. Rev.* **2007**, *36*, 198–210; b) F. Corbellini, A. Mulder, A. Sartori, M. J. W. Ludden, A. Casnati, R. Ungaro, J. Huskens, M. Crego-Calama, D. N. Reinhoudt, *J. Am. Chem. Soc.* **2004**, *126*, 17050–17058; c) N. J. Burke, A. D. Burrows, M. F. Mahon, J. E. Warren, *CrystEngComm* **2006**, *8*, 931–945.

[22] C. Bianchini, A. Meli, W. Oberhauser, A. M. Segarra, C. Claver, E. J. G. Suarez, *J. Mol. Catal. A* **2007**, *265*, 292–305.

[23] P. W. N. M. van Leeuwen, *Appl. Catal. A* **2001**, *212*, 61–81.

[24] E. Lindner, R. Fawzi, H. A. Mayer, K. Eichele, W. Hiller, *Organometallics* **1992**, *11*, 1033–1043.

[25] a) W. L. Steffen, G. J. Palenik, *Inorg. Chem.* **1976**, *15*, 2432–2439; b) R. J. van Haaren, K. Goubitz, J. Fraanje, G. P. F. van Strijdonck, H. Oevering, B. Coussens, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Inorg. Chem.* **2001**, *40*, 3363–3372; c) P. Dierkes, P. W. N. M. van Leeuwen, *J. Chem. Soc. Dalton Trans.* **1999**, *10*, 1519–1530.

[26] a) B. Punji, J. T. Mague, M. S. Balakrishna, *Inorg. Chem.* **2007**, *46*, 10268–10275; b) J. W. Perich, R. B. Johns, *Synthesis* **1988**, *2*, 142–144.

[27] a) P. Job, *Ann. Chim.* **1928**, *9*, 113–203; b) M. T. Blanda, J. H. Horner, M. Newcomb, *J. Org. Chem.* **1989**, *54*, 4626–4636.

[28] a) A. P. Bisson, C. A. Hunter, J. C. Morales, K. Young, *Chem. Eur. J.* **1998**, *4*, 845–851.

Received: January 31, 2011
Published online: June 9, 2011

